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The Effect of Acetyl Content of Glucomannan on its Sorption onto Cellulose and on its Beater Additive Properties

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THE EFFECT OF ACETYL CONTENT OF GLUCOMANNAN ON ITS SORPTION ONTO CELLULOSE AND ON ITS BEATER ADDITIVE PROPERTIES

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SUMMARY

Studies concerning the sorption of hemicelluloses onto cellulose substrates or their influence on papermaking properties have not, generally, been concerned with the behavior of functional groups. Naturally occurring glucomannans contain significant acetyl substitution. Because removal of these groups affects glucomannan solubility and may also influence glucomannan pulping and papermaking behavior, the effect of glucomannan acetyl content on its sorption and papermaking properties was chosen as the basis for this thesis investigation.

Attention was also directed toward evaluating selective sorption due to molecular weight and polymer exchange at the cellulose-glucomannan interface in this hydrogen-bonded system.

In order to minimize variables and provide the most simple system possible, Tubera salep glucomannan and beaten classified cotton linters were utilized in the investigation. Differences in supernatant concentrations were used to determine quantities sorbed. Selective sorption due to molecular weight and polymer exchange were evaluated by determining the intrinsic viscosities of samples isolated from the supernatant solutions. These samples were obtained at intervals during sorption runs. The effect of glucomannan acetyl content on papermaking properties was studied by comparing two pulps containing similar amounts of acetylated and deacetylated glucomannan with a cotton-linter control pulp.

It was established that the removal of glucomannan acetyl groups leads to decreased water solubility, a higher rate of sorption onto a cotton-linter substrate, an earlier mass equilibrium, and a higher specific sorption for a given amount of added glucomannan. While the sorption of the acetylated polymer reached a maximum specific sorption of approximately 7.5% with increasing glucomannan addition, the sorption of the deacetylated glucomannan was a function of the

amount added. It is believed that the acetylated glucomannan is restricted to monolayer sorption, but that multilayer sorption occurs with the deacetylated polymer.

A diffusion-controlled sorption mechanism is indicated by the fact that smaller molecules are sorbed initially with both glucomannans. Polymer exchange was exhibited by the acetylated glucomannan and involved periods of several days. In the case of the deacetylated glucomannan, polymer exchange either did not occur or was characterized by an extremely slow rate.

By varying the amounts of glucomannan and times of sorption, two pulps were prepared containing equal amounts of either acetylated or deacetylated glucomannan. The pulp containing the deacetylated polymer exhibited higher tearing strength, breaking length, and tensile energy absorption value, as well as greater stretch, at any given freeness level. This indicates that the presence of acetyl groups decreases the efficiency of the hemicellulose.

A discussion section is presented in which experimental results are used to speculate on sorption mechanisms, polymer exchange, the behavior of glucomannan during pulping and refining, and the role of this hemicellulose as a beater additive.

The acetyl groups on the glucomannan are quite bulky and prevent the polymer from crystallizing. It is felt that this polymer exhibits monolayer sorption with only a portion of each molecule actually hydrogen bonded to the cellulose surface. It is also believed that this layer is an intermediate between undissolved and dissolved material. The deacetylated polymer exhibits multilayer sorption; and, rather than a transition layer, an ordered surface is expected. A comparison of the rates of polymer exchange for four different systems indicates that the rate of polymer exchange is closely related to the heat of sorption or tenacity of the polymer-sorbent interaction.

The locations of glucomannan in kraft and sulfite fibers are explained in terms of glucomannan acetyl content. During kraft cooking the glucomannan is dissolved, deacetylated, and, under proper conditions, sorbed onto the fiber surfaces. In the cooking of sulfite pulps the glucomannan is not deacetylated, dissolves to a large extent into the cooking liquor, and is not resorbed. The fact that the glucomannan remaining in sulfite pulp is uniformly distributed through the cell wall supports this theory. Increased glucomannan retention with two-stage sulfite cooking is attributed to removal of acetyls (but not dissolution of the glucomannan) during the slightly alkaline precook which renders the glucomannan insoluble during the subsequent acid cook.

The deacetylated glucomannan, with more available hydroxyls, is apparently a more efficient beater additive. Increased strength properties are attributed to increased fiber bonding, improved bond distributions, and less fiber deterioration.

INTRODUCTION

The sorption of polysaccharides onto cellulose substrates has been the subject of many studies in recent years. While specific gums, starch, and mixtures of hemicelluloses have been investigated, the sorption behavior of specific hemicelluloses and the effects of their functional groups have received little attention. Mechanisms by which hemicelluloses influence papermaking properties of cellulose fibers are not fully understood. A better understanding of hemicellulose sorption and how these hemicelluloses influence papermaking properties may be gained by evaluating the effects of functional groups present in the hemicelluloses.

Recent findings concerning the acetyl groups associated with glucomannans make this functional group an attractive subject for further study. Katz (1), after isolating and determining the structure of a natively acetylated glucomannan, found the physical properties of the deacetylated polymer to be strikingly different from the acetylated polymer. It has also been demonstrated that a neutral or alkaline pretreatment leads to increased retention of glucomannan during acid-sulfite pulping. This pretreatment leads to a higher degree of bonding between the cellulose and glucomannan by removing bulky acetyl groups from the glucomannan.

The purpose of this experimental investigation was to study the effect of acetyl content on the sorption and papermaking properties of a glucomannan. A portion of the experimentation was concerned with detecting the presence of preferential sorption due to molecular weight and possible polymer exchange at the cellulose surface.

THE SORPTION OF POLYSACCHARIDES BY CELLULOSE

In many phases of pulping and papermaking, the role of polysaccharide sorption is quite prominent. Hemicelluloses dissolved from the wood during early pulping stages can sorb onto the surface of the cellulose fibers, and beater additives such

as starch and natural gums are normally retained by a sorption mechanism. A brief review of polysaccharide sorption studies will emphasize the need for further research concerning hemicellulose sorption.

Shriver (2) studied the sorption of water-soluble cellulose ethers by cellulose fibers. This was one of the earliest studies concerned with measuring the quantity of polysaccharide actually sorbed. Times approaching 180 hours were required to reach equilibrium. The sorption was found to be quite irreversible with respect to concentration. An increase in temperature led to an increase in equilibrium sorption while a decrease in temperature led to some desorption. Pearl (3) investigated the rate of sorption of amylose by wood pulps. He found that the sorption continued slowly for a long period and that eventually all the amylose was removed from solution. The sorption was irreversible with respect to concentration but some desorption occurred when samples were suspended in water at temperatures above the original sorption temperature. The quantity of amylose sorbed at any time was proportional to the initial concentration. Pearl postulated a sorption mechanism with amylose depositing on both cellulose and previously sorbed amylose as a result of hydrogen bonding.

Early studies of the sorption of guar and locust-bean gum were carried out by Gruenhut (4) and Keen and Opie (5). Russo (6) mentions unpublished work of Webb, Morse, and Swanson which indicates that the sorption of locust-bean gum is quite rapid. This sorption was found to be quite irreversible, also, as no desorption occurred upon extensive Soxhlet extraction of a sorbed pulp with distilled water. Russo (6) studied the effects of several system variables on the sorption and rate of sorption of a partially methylated locust-bean gum. A radiochemical tagging method was utilized to determine sorption. He hypothesizes multilayer sorption of the gum with multiple hydrogen bonding leading to a high degree of irreversibility. He also points out that the migration of the gum into the fiber is quite unlikely.

Hemicellulose sorption studies have been carried out both with samples isolated from cooking liquors and samples extracted from holocellulose. Yllner and Enstrom (7) studied the sorption of pentosans removed from birch and sprucewood during early stages of a kraft cook. Pentosans were sorbed from the cooking liquor onto cotton, cotton linters, and bleached-sulfite fibers. The quantity of hemicellulose sorbed increased with time and was related to the initial pentosan content of the liquor. The sorption continued until the pentosan content of the liquor became negligible. The sorption was irreversible with respect to concentration and approximately 20% of the sorbed pentosans could not be removed by a one-hour extraction with aqueous (10%) sodium hydroxide.

Clayton and Stone (8) studied the redeposition of xylans during kraft pulping. A tritium labeled white-birch xylan was used to demonstrate that xylan dissolved from hardwoods in the early stages of an alkaline cook may be redeposited on the fibers at a later stage.

Most (9) investigated the sorption of slash-pine hemicelluloses onto alpha-cellulose pulp. Four fractions were isolated by successive extractions of the hemicellulose from a chlorite holocellulose with 1, 4, 7, and 16% potassium hydroxide. Each fraction was a mixture of glucomannans and xylans. Quantities sorbed were determined by labeling a portion of each hemicellulose fraction with carbon-14 through the Kiliani cyanohydrin reaction.

No true sorption equilibrium was noted after 240 hours, but the rate curves became nearly level after 48 hours. The mannan-rich fraction sorbed at a higher rate and reached a higher pseudoequilibrium* sorption level than the xylan (or

*Most used this term to describe the mass of material sorbed after 48 hours.

carboxyl)-rich fraction. Sorption was studied at pH values of 10 and 4.5. Both the level and rate of sorption were higher at a pH of 4.5. Most attributed this either to an electrolyte effect (the increased solubility of carboxyl-containing xylans at higher pH) or the greater solubility of hemicelluloses in base. The effects of the other system variables such as temperature and concentration were also studied.

Walker (10) has investigated the effect of the uronic acid carboxyl of 4-O-methylglucuronoarabinoxylan on the solubility in water, sorption onto cellulose, and papermaking properties of this hemicellulose. It was shown that a decrease in carboxyl content led to decreased solubility in water and increased sorption in water of the reduced polymer on a beaten classified cotton-linter pulp. The fact that a decrease in carboxyl content led to increased sorption would help to explain the higher sorption level of the mannan-rich (carboxyl-poor) fraction in Most's study. Walker also noted that the sorption was selective with respect to molecular size, the longer chain molecules being preferentially sorbed. As Walker's objective was to study the effect of the carboxyl group on the papermaking properties of the xylan, no rate measurements were made.

Eriksson, Samuelson, and Viale (11) isolated degraded hemicelluloses from spruce-sulfite digester liquor and studied their sorption onto cellulose fibers. Analysis of the hemicellulose mixture indicated xylans and acetylated glucomannans were present, the latter predominantly. Results of the sorption study closely paralleled Most's findings. It is of interest to note that these authors found the sorption level to remain relatively constant over a pH range of 2 to 11.5. While the quantity sorbed over this pH range remained constant, it does not seem likely that the composition of the sorbed fraction would also remain constant. Clayton and Phelps (12) have studied the rates of sorption of a birch xylan and a spruce glucomannan onto wood fibers in 0.02N alkali at four temperatures. By labeling the glucomannan with carbon-14 and the xylan with tritium, they could measure the

sorption rate of each hemicellulose, alone or together. In both cases, the rates of sorption of the glucomannan were about twice those for the xylan. The lower rate of sorption of the xylan is ascribed to the presence of uronic-acid carboxyl groups.

While a few of these studies are concerned with the sorption behavior of individual hemicelluloses, little attention is paid to substituted groups. Only in Walker's investigation (10) was it demonstrated that xylan carboxyl content markedly affects the solubility and sorption of this polymer. Walker also found that fractions of higher molecular weight are preferentially sorbed at equilibrium levels. Although Walker's study indicated the sorption behavior of an individual hemicellulose and a substituent, no rate studies or equilibrium determinations were carried out. While Most (9) and Eriksson, et al. (11) carried out extensive sorption studies, little information could be obtained regarding selective sorption of specific hemicelluloses and molecular sizes or the role of substituents.

Naturally occurring glucomannans contain significant acetyl substitution (1). The presence of these groups greatly influences the solubility and other properties of this hemicellulose. Ionization of the xylan carboxyls and cleavage of the glucomannan acetyl groups are both functions of the pH of the system. It was the initial intention of this writer to study the effect of pH on the sorption behavior of both these hemicelluloses individually and as mixtures. However, it was decided that the magnitude of this investigation would lead to difficulties. Therefore, this study was limited to the effect of acetyl content on glucomannan sorption with an added study of the influence of these groups on papermaking properties of the glucomannan-sorbed pulps.

PROPERTIES OF GLUCOMANNANS

Glucomannans are the predominant hemicelluloses associated with softwoods. They are heteropolymers of β-1,4 linked D-mannose and D-glucose in proportions ranging from 2.5 to 4.0:1 (1). Small amounts of galactose, appearing as terminal nonreducing end groups linked to the main chain by α-1,6 glycosidic bonds, have also been reported (13). Degrees of polymerization are cited for alkali-extracted glucomannans ranging from 70 to 130 (14).

Extraction with alkali cleaves any ester groups that might be associated with the glucomannan. Hagglund, et al. (15) found that dimethylsulfoxide (DMSO) could be used to extract hemicelluloses without affecting naturally occurring acetyl groups. A combination of a physical pretreatment, to increase accessibility, with DMSO extraction has led to the isolation of natively acetylated glucomannans (1, 16, 17).

Meier (17) and Katz (1) have found acetyl contents of 5.95 and 5.86% for glucomannans from Scots and Parana pine, respectively. Meier indicated that the acetyls were substituted on the secondary hydroxyls of the mannose units, while Katz showed that they were substituted on only the C_3 hydroxyls of both the glucose and mannose units. The molecular weight of Katz's natively acetylated glucomannan was comparable to alkali-extracted glucomannans.

Katz saponified (deacetylated) a portion of his acetylated glucomannan in order to compare it with the natively acetylated form. The acetylated glucomannan remained water soluble, appeared isotropic to polarized light, and gave a diffuse x-ray diffractogram even after aging for over a year. The deacetylated glucomannan, on the other hand, became insoluble in dilute alkali, showed birefringence under polarized light, and gave an x-ray pattern indicative of an ordered structure upon aging. Katz concluded that the presence of acetyl groups restricts the

molecules to random orientation due to the bulkiness of these groups compared with hydroxyls, while the removal of the acetyl groups may lead to increased lateral order through hydrogen bonding.

BEHAVIOR OF GLUCOMANNANS DURING PULPING

Glucomannans represent 50 to 75% of the total hemicelluloses in softwoods. These hemicelluloses can represent up to 30% of the wood and less than one-third of this material is retained with conventional pulping methods (18). The fate of the glucomannan is greatly influenced by the pulping conditions. The galactose units are acid labile and are, therefore, removed in acid-sulfite or prehydrolyzed-kraft pulps. Acetyl groups are also greatly affected by pH differences in the pulping methods.

The acetyl groups are relatively stable during acid-sulfite pulping. It is felt that the presence of these groups hinders hydrogen bonding and leads to dissolution of the glucomannan into the cooking liquor (18). Sorption of the dissolved polymer onto the surface of the cellulose may occur to a small extent; but, in general, it is degraded and lost. During kraft pulping the glucomannan undergoes peeling and high-temperature scission along with the cellulose. Removal of alkali-labile acetyl groups leads to decreased solubility in the cooking liquor and increased sorption onto the cellulose (as compared to acid-sulfite cooking). However, the high peeling rate decreases retention. Pulping innovations have been developed in recent years to increase both kraft and sulfite yields by retaining more glucomannan. Sodium borohydride addition to kraft cooking liquors or its use as a pretreatment reduces the carbonyl ends of the glucomannan and retards peeling. Neutral or alkaline precooks increase glucomannan retention during acid sulfite pulping.

Annergren and Rydholm (19, 20) were, perhaps, the first investigators to recognize the value of a neutral treatment prior to acid-sulfite pulping. Higher yields were obtained in these two-stage cooks. The authors postulate that the glucomannans may become crystalline and thus more resistant or that they may become sorbed either on the surface or within the cellulose microfibrils during the alkaline precook. Annergren, et al. (16) later completed a sequence of experiments which demonstrated that the stabilization reaction was not associated with lignin, that fairly high pH was necessary to obtain stabilization, and that a deacetylation of the glucomannan was involved. Recently, Croon, et al. (21) showed that the stability of the glucomannan to acid hydrolysis in the second stage is proportional to the degree of deacetylation in the first stage. Deacetylation in the first stage was found to be a function of pH, time, and temperature. The authors postulated that the cleavage of acetyls gives the glucomannan a more ordered structure and increased resistance to acid hydrolysis.

Katz (1) has interpreted glucomannan stability on the basis of his comparison of acetylated to deacetylated glucomannan. He proposes that in the alkaline precook (pH of 8-9) the O-acetyl groups are cleaved and the glucomannan molecules become highly oriented with respect to each other and the cellulose. On acidification, some chain cleavages occur followed by sorption of the deacetylated glucomannan molecules onto the cellulose microfibrils. The net result is an increase in the degree of lateral order for the polymer with an increase in the resistance of the glucomannan to acid hydrolysis.

THE ROLE OF HEMICELLULOSE IN PAPERMAKING

Not only may glucomannan acetyl content affect the sorption characteristics, but it may also influence the way in which this hemicellulose affects papermaking properties. It is well known that the presence of hemicelluloses contributes to

the bonding or strength properties of pulps. However, the mechanisms by which hemicelluloses influence the papermaking properties of cellulose are not fully understood. In particular, the role of substituted groups has received little attention.

Thompson, et al. (22) studied the factors influencing the effectiveness of hemicelluloses as beater additives. The authors found the softwood hemicelluloses superior to those in hardwood for improving strength properties. It was postulated that the hemicelluloses act as interfiber adhesives, contributing to the paper strength by virtue of their ability to improve bonding between fibers. In order for the hemicellulose molecules to enhance fiber-to-fiber bonding, they must first be sorbed onto the surface of the cellulose fibers. The kind of bonds involved in this specific adhesion are secondary valence bonds between the highly polar hydroxyls of the hemicellulose and those on the fiber surface. The hemicellulose's degree of polymerization and cohesive strength are important as the hemicellulose must link fibrils. These authors theorized that the mannans, with three hydroxyls per monomer unit, accounted for the greater effectiveness of the softwood hemicelluloses. (The hardwood hemicelluloses were predominantly xylans.)

Walker (10) has shown that for the same level of sorbed xylan, increased carboxyl content of the xylan leads to better papermaking properties. This effect was attributed to an increased affinity (due to more hydrophilic groups) of the carboxyl-rich xylan for water and the accompanying increased flexibility and swelling.

It has been pointed out by Swanson (23, 24) that swelling and flexibility are important factors in fiber bonding. In order for bonding to occur, close proximity is necessary. Better contact can be obtained with plasticizing and swelling of the fiber. The action of the hemicellulose to increase the hydrophilic nature of the fiber and enhance the above effects is one way hemicelluloses influence papermaking properties. The hemicelluloses may also act as a bridge between fibrils on adjacent fibers and, in a sense, bring the fibers closer together.

Bletzinger (25), Aiken (26), and Higgins, et al. (27) found a similar effect with the substitution of small amounts of hydrophobic acetyl groups onto cellulose pulps. At low additions, the affinity of the cellulose for water was increased and papermaking properties improved. Bletzinger explains this effect as an "opening-up" of the cellulose structure, making more hydroxyls available for hydration and swelling. The addition of a small amount of acetyl groups onto the surface of the fibers may reduce the attraction between surface micelles and permit intermicellar spaces to be opened more readily during mechanical treatment. Larger acetyl additions leading to acetyl groups throughout the structure, though, would prevent water from entering and solvating the fibers, causing decreased hemicellulose efficiency.

Hydrophilic substitution also benefits papermaking properties of cellulose. Studies on the substitution of carboxymethyl groups (which are more hydrophilic than hydroxyls) indicate that low substitutions of these groups give higher physical strength with less beating (28-30).

PRESENTATION OF HYPOTHESES AND GOALS OF THESIS INVESTIGATION

In considering the preceding discussions, it is fairly obvious that the acetyl groups present in naturally occurring glucomannans play a major role in the properties and behavior of this hemicellulose. It can immediately be hypothesized that the removal of acetyl groups leads to an increase in the rate of glucomannan sorption. Evidence presented does not clearly indicate whether the amount of glucomannan sorbed at equilibrium is affected by the presence of acetyl groups. Experiments were carried out to determine how the presence of acetyl groups affects both the rate of glucomannan sorption and the amount sorbed at equilibrium.

In addition to rate and equilibrium sorption studies, selective sorption due to molecular weight and polymer exchange at the cellulose interface were evaluated. Emery (31) has studied the polymolecularity of adsorption in a physical system (with

no hydrogen bonding) and found that smaller molecules were preferentially adsorbed initially, but were subsequently displaced by larger molecules. This investigation extends Emery's study to a hydrogen-bonded system.

The effects of acetyl content on papermaking properties are not as easily predicted as the effects on sorption. The presence of the more hydrophobic acetyl groups could be considered to have a deleterious effect as the number of hydroxyls present in the hemicellulose is decreased; or considering the results of Bletzinger (25), an increase in effectiveness could be predicted due to the low acetyl content making the hemicellulose more receptive to bonding. It should be noted here that the presence of hemicelluloses leads to the same changes in a pulp as low acetyl substitution. So, in a sense, by varying the acetyl content of the glucomannan a structure influencing the cellulose is varied, rather than the cellulose itself. Therefore, experimental work was also concerned with determining the influence of glucomannan acetyl content on this hemicellulose's contribution to refining and strength properties of pulps.

EXPERIMENTAL

SOURCE OF GLUCOMANNAN

Large quantities (approximately 300 g.) of natively acetylated glucomannan were required for this investigation. It was also quite important that the material be as pure as possible. While essentially pure glucomannans have been isolated from wood, the methods currently employed are not satisfactory for large yields.

Juers (32) recently demonstrated that the water-soluble reserve polysaccharide contained in the tubers of several species of Orchis and Eulophia is a high molecular weight (240,000) acetylated glucomannan. Husemann (33) found that a natural enzyme contained in the tuber reduces the polymer's molecular weight upon dissolution of the tuber in water. By allowing this enzyme to react, large quantities of pure glucomannan can be obtained with a glucose-to-mannose ratio and molecular weight comparable to wood glucomannans. The acetyl content is somewhat lower in the Tubera salep than has been reported for softwoods. Husemann (33) reports 3.5% while Juers (32) found slightly under 3%. These acetyl groups are not removed by the enzyme.

ISOLATION OF ACETYLATED GLUCOMANNAN

Although the water extract of powdered Tubera salep provides an excellent source of pure acetylated glucomannan[1], the molecular weight of this polymer is much higher than that of glucomannan found in wood. Fortunately, an enzyme which attacks β-1,4 links without affecting other properties is extracted along with the glucomannan. It was necessary to determine how long to allow the enzyme to react. Because information is available on the 0.5M cupriethylenediamine (cuene[2]) intrinsic

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[1] The expression, acetylated glucomannan, will be used to signify natively acetylated polymer, i.e., 2.75% acetyl content.

[2] Unless otherwise noted, the abbreviation cuene will refer to 0.5M cupriethylenediamine.

viscosity of wood glucomannans, it was decided to allow the glucomannan to degrade until the desired cuene intrinsic viscosity was reached. Linnell (35) found an intrinsic viscosity of 0.43 dl./g. for a wood glucomannan with a molecular weight of about 17,000 and Katz (1) reported an intrinsic viscosity of 0.35 for a molecular weight of about 12,000. In a literature review, Katz also listed intrinsic viscosities varying from 0.22 to 0.56 for wood glucomannans. While this procedure provided a desired end point for the degradation, it did not provide an immediately obtainable measurement of intrinsic viscosity. After examining several possibilities (see Appendix I), it was found that a reasonable relationship existed between cuene intrinsic viscosity and the period of fall for ball "B" through the solution in a Hoeppler viscometer. Periods of fall with ball "B" of from 10 to 30 seconds in a 2% solution corresponded to respective intrinsic viscosities of from 0.4 to 0.6. This result was utilized to produce a large batch of glucomannan.

In a constant temperature humidity room (70°F., 50% R.H.), 600 grams of powdered Tubera salep were dispersed in 30 liters of distilled water. A Lightnin' mixer was used to agitate the solution during, and for two hours after, the addition of the salep. A few drops of water saturated with xylene were added to the surface to retard microorganism growth. After 44 hours of water extraction, centrifugation of the solution was begun. Both the Beta-fuge and a laboratory centrifuge were utilized to remove insoluble residue. This batch operation required 16 hours. Glucomannan degradation was then closely monitored by measuring the period of fall on the Hoeppler viscometer for ball "B" through samples withdrawn from the batch. After 100 hours an undetermined amount of ptyalin was added to the solution in order to degrade any starch which might be present. Finally, prior to precipitation, the solution was continuously centrifuged on the Sharples Super Centrifuge at 43,000 r.p.m. and a flow rate of 500 ml./min. When the period of fall for ball "B" reached 18 seconds, the enzyme action was quenched, and the glucomannan was precipitated, by pouring the solution into acetone.

The 30 liters of solution were poured into 90 liters of acetone, during which time the acetone was agitated by an air-driven mixer. The solution was agitated for an additional two hours, and then left for 36 hours with occasional stirring. The precipitated glucomannan was then isolated by siphoning most of the acetone-water mixture and filtering off what remained. The glucomannan was next redispersed in 20 liters of acetone and left for 24 hours. This was then replaced with petroleum ether and left for 48 hours. Finally, the glucomannan was isolated by filtering off as much of the ether as possible and then drying under vacuum for five days. The product contained large amounts of plastic horny material.

The product was, therefore, redissolved in eight liters of distilled water. A newly developed method (36) of freeze-exchanging was modified to isolate the polymer. The solution was poured into dialysis bags, frozen, and after bag removal, placed into three volumes of chilled absolute ethanol. The water then dissolved, rather than melting, from the solution into the alcohol, leaving porous "sponges" of glucomannan. This process took about six hours. The sponges were then drained, suspended in acetone overnight, drained again, suspended in petroleum ether overnight, and air dried at 70°F. and 50% R.H. The product was quite uniform, resembling a freeze-dried one. The procedure used to degrade the glucomannan is illustrated schematically in Fig. 1. Period of fall data for ball "B" and intrinsic viscosity data used in this figure are drawn from Appendix I.

PROPERTIES OF THE GLUCOMANNAN

The experimental procedures used to evaluate the properties of the glucomannan find use throughout the experimental section of this thesis. For this reason, they are consolidated in Appendix II and will only be mentioned briefly in the body of the thesis.

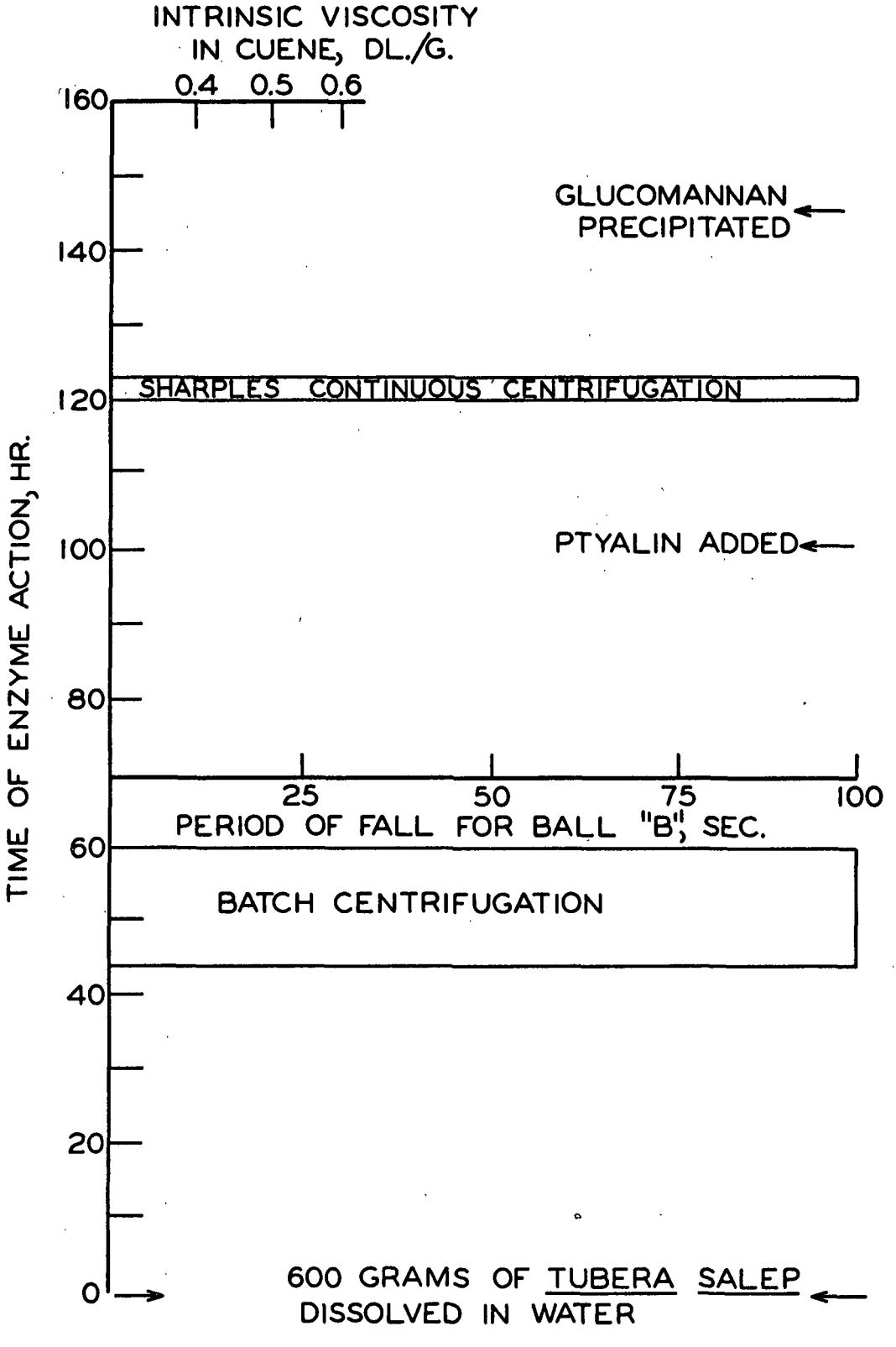

Figure 1. Schematic Diagram of Batch Degradation

The properties of the glucomannan are listed in Table I. Acetyl content was determined according to Whistler and Jeanes (37), intrinsic viscosity was measured in both 1.0% aqueous sodium chloride and cuene, and the number average molecular weight was determined in 1.0% aqueous sodium chloride on the high-speed membrane osmometer. Quantitative sugar content was determined by the Analytical Department at The Institute of Paper Chemistry according to the Saeman technique (38). Institute method 25 was used to determine uronic acid content. Also presented in Table I are Juers's (32) measurements of ash content, nitrogen content, and optical rotation.

TABLE I

PROPERTIES OF THE GLUCOMANNAN

Property	Value	Reference
Acetyl content, %	2.75 ± 0.05	Appendix II
Intrinsic viscosity, dl./g.		Appendix II
Cuene	0.419	
1% NaCl	0.985	
Number average molecular weight	15,120	Appendix II
Sugar content, %		Analytical Department (38)
Glucan	25.7 ± 0.5	
Mannan	67.7 ± 2.0	
Galactan	0.5 ± 0.1	
Polyuronides, %	2.8 ± 0.1	Institute Method 25
Ash content	None	Juers (32)
Nitrogen content, %	0.1	Juers (32)
Optical rotation in 6% NaOH	$[\alpha]_D^{25} = 43.3°$	Juers (32)

Juers found no variation in sugar content with molecular weight. Sephadex fractions examined by this writer demonstrated no variation in acetyl content with molecular weight.

Juers (32) carried out a graded acid hydrolysis on the glucomannan and the hydrolyzate contained all the possible mono- and disaccharides, and one of the possible trisaccharides that would be expected from a graded hydrolysis of a wood glucomannan.

FRACTIONATION OF THE GLUCOMANNAN

The glucomannan was fractionated on a Sephadex column in order to examine the distribution of this polymer and to determine whether acetyl distribution is a function of molecular weight. These fractions were also desired so that a relationship could be established between number average molecular weight and intrinsic viscosity.

A water solution of glucomannan (five grams) was fractionated on a G-75 Sephadex column. Sephadex is a cross-linked dextran which fractionates on a molecular sieve principle. G-75 is designed for materials in the 30,000 to 40,000 molecular weight range, but was the best gel available for the fractionation. The fractionation was carried out at 34°F. on an automatic fractionator which changed tubes every 20 minutes. Four-hundred tubes were collected. An anthrone color reaction was employed to determine the approximate weight distribution of the polymer and insure even division of the glucomannan into fractions. The tubes were combined into 21 fractions and the glucomannan fractions were isolated by the freeze-drying technique.

INTRINSIC VISCOSITY--MOLECULAR WEIGHT RELATIONSHIPS

A portion of this thesis investigation was concerned with examining the molecular character of unsorbed polymer, and it was felt that these results should be discussed in terms of molecular weight instead of the directly-measured intrinsic viscosity. Because 1.0% aqueous sodium chloride was used for determining intrinsic

viscosities on acetylated polymer and cuene was used for the deacetylated polymer, equations converting these quantities to number average molecular weight would prove invaluable.

Both number average molecular weights and intrinsic viscosities were determined in 1% aqueous sodium chloride on five acetylated Sephadex fractions and the glucomannan starting material. Details of these procedures and extrapolations used to determine molecular weight are given in Appendix II. The results are presented in Table II.

TABLE II

INTRINSIC VISCOSITIES AND MOLECULAR WEIGHTS FOR GLUCOMANNAN FRACTIONS

Sample	Intrinsic Viscosity, dl./g.	Number Average Molecular Weight
Starting material	0.986	15,120
Fraction 2	1.090	18,250
4	1.051	17,500
8	0.976	15,020
12	0.905	13,970
15	0.840	11,950

Figure 2 depicts the log-log plot of molecular weight versus intrinsic viscosity and a least squares treatment provides the relationship:

$$[\eta]_w = 1.516 \times 10^{-3} M_n^{0.699} \qquad (1)$$

where

$[\eta]_w$ = intrinsic viscosity in 1% sodium chloride

M_n = number average molecular weight

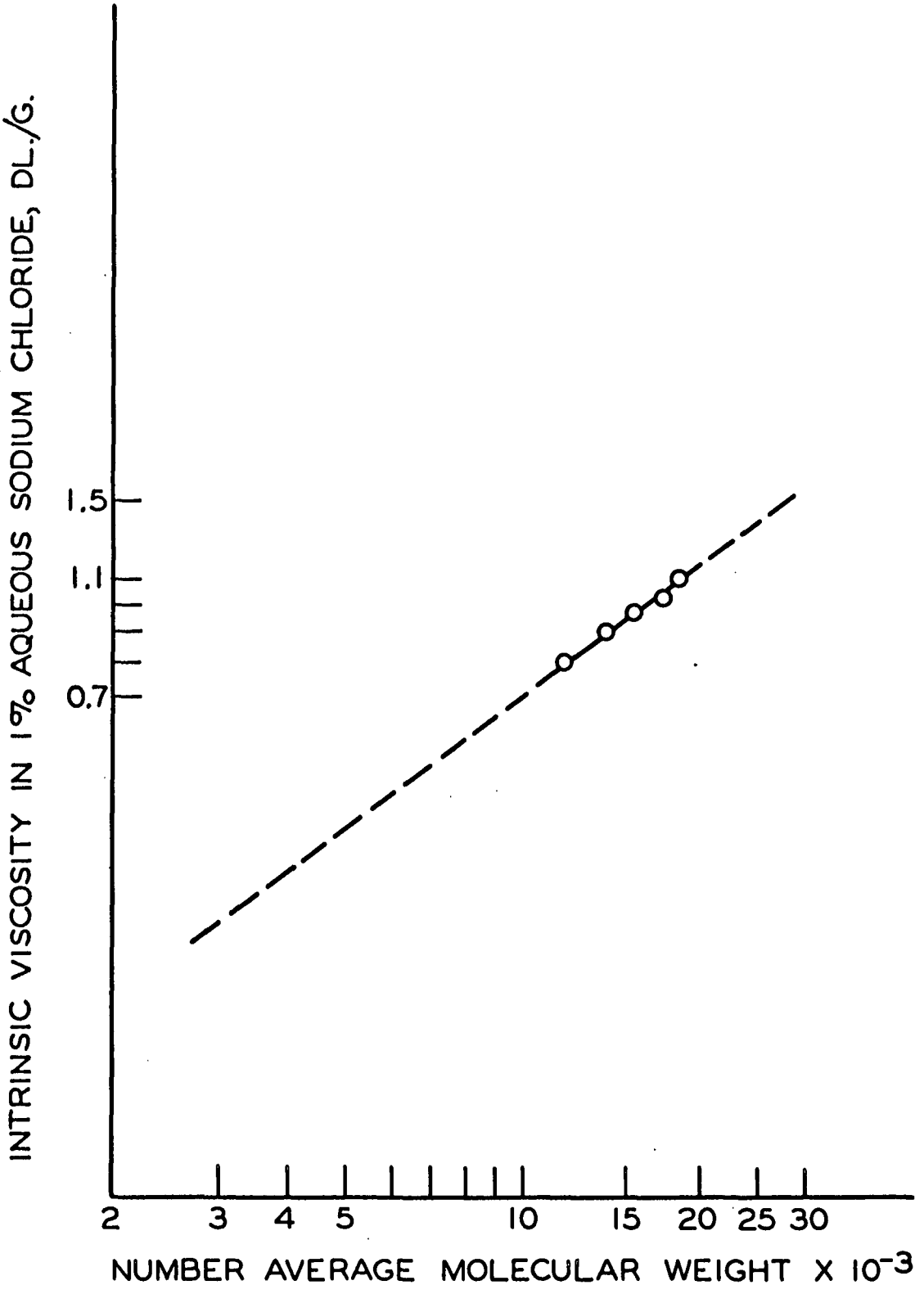

Figure 2. Log-Log Plot of Intrinsic Viscosity Versus Number Average Molecular Weight

This equation can be rearranged to the more useful form:

$$M_n = 16{,}150\ [\eta]_w^{1.493} \qquad (2).$$

A relationship between cuene intrinsic viscosity and number average molecular weight was estimated by determining the ratio of intrinsic viscosity in 1.0% sodium chloride to that in cuene and substituting it into Equation (2). Viscosity measurements were made in both solvents on the glucomannan starting material and two other combined glucomannan samples. Those results are shown in Table III.

TABLE III

INTRINSIC VISCOSITY MEASUREMENTS IN CUENE AND 1% SALT SOLUTION

Sample	Intrinsic Viscosity in 1% Salt Solution, dl./g. ($[\eta]_w$)	Intrinsic Viscosity in Cuene, dl./g. ($[\eta]_c$)	$[\eta]_w/[\eta]_c$
Starting material	0.985	0.419	2.351
Some combined Sephadex fractions	0.960	0.395	2.430
Some combined supernatant glucomannan from sorption Run K	1.150	0.500	2.300

By substituting the average ratio (2.360) into Equation (2), Equation (3) is obtained:

$$M_n = 58{,}188\ [\eta]_c^{1.493} \qquad (3).$$

This equation allows the calculation of molecular weight from cuene intrinsic viscosity data.

POLYDISPERSITY OF THE GLUCOMANNAN

While the Sephadex fractions proved quite useful for establishing the relationship of molecular weight to intrinsic viscosity, it is felt that the short column

length and large sample size combined to provide poor resolution of the glucomannan. Poor resolution would imply a more narrow distribution than is actually present.

Intrinsic viscosity values in aqueous 1.0% sodium chloride and number average molecular weights, as calculated from Equation (2), are given in Table IV. A weight to number average molecular weight ratio $\underline{M}_w/\underline{M}_n$, can be estimated from the fractionation data. The definitions of these quantities may be written (39):

$$M_w = \Sigma w_i M_i \tag{4}$$

and

$$M_n = 1/\Sigma(w_i/M_i) \tag{5}$$

where $\underline{w}_i$ is the weight fraction of species with molecular weight $\underline{M}_i$. The ratio of $\underline{M}_w$ to $\underline{M}_n$ can therefore be written:

$$M_w/M_n = [\Sigma(w_i M_i)][\Sigma(w_i/M_i)] \tag{6}.$$

This ratio may also be estimated from viscosity data (39) with Equation (6) becoming:

$$M_w/M_n = [\Sigma(w_i[\eta]_i)][\Sigma(w_i/[\eta]_i)] \tag{7}.$$

Equation (6), based on molecular weight, gives a ratio of 1.27, while Equation (7) based on intrinsic viscosity produces a value of 1.10. These values compare favorably with the 1.33 ratio found by Walker (10) on a xylan and indicate a narrow distribution. It is anticipated, however, that the distribution is actually wider due to poor resolution; but the ratio obtained is significant in that it is comparable to values determined similarly on a hemicellulose.

TABLE IV

GLUCOMANNAN FRACTION DATA

Sephadex Fraction No.	Weight Fraction	Intrinsic Viscosity 1.0% NaCl, dl./g.	No. Average Molecular Weight Calculated	Measured
2	0.08253	1.090	18,363	18,250
3	0.05503	1.080	18,120	--
4	0.04828	1.051	17,394	17,500
5	0.05941	1.021	16,667	--
6	0.07046	1.011	16,408	--
7	0.06402	0.999	16,134	--
8	0.05183	0.976	15,569	15,020
9	0.04991	0.961	15,229	--
10	0.04823	0.957	15,116	--
11	0.05266	0.923	14,325	--
12	0.06815	0.905	13,905	13,970
13	0.07815	0.857	12,823	--
14	0.06755	0.821	12,032	--
15	0.06612	0.804	11,660	11,950
16	0.05436	0.722	9,932	--
17	0.02348	0.714	9,771	--
18	0.02209	0.666	8,802	--
19	0.02234	0.587	7,284	--
20	0.00892	0.191	1,357	--
21	0.00646	0.106	565	--

PREPARATION OF THE COTTON LINTER SUBSTRATE

The cellulose substrate used in this study had to have negligible hemicellulose content and sufficient surface area so that sorption is enhanced. Negligible cellulose dissolution was also necessary as quantities sorbed were determined by changes in supernatant concentration. Dissolution of cellulose would also interfere with intrinsic viscosity determinations. Beaten and classified cotton linters as described by Walker (10) were, therefore, used in this study. Most (9) used an unfractionated alpha-pulp for his study of hemicellulose sorption and found a high degree of cellulose dissolution, while Walker noted only negligible cellulose solution with the classified cotton-linter substrate.

Acetate-grade cotton linters (Type 7AY 500-2 Bulkipulp) were obtained from the Cellulose Chemistry Department at The Institute of Paper Chemistry. The linters were soaked in water for 24 hours prior to refining. A two-hour beating period in a Valley laboratory beater (with a load of 5500 g.) lowered the Schopper-Riegler freeness* from 900 to 460 ml. The refined pulp was then processed through a Bauer-McNett classifier with the 20, 28, 48, and 65-mesh screens. The fraction passing the 65-mesh screen was discarded. A batch process was used, 20 grams of pulp being fractionated for a ten-minute period.

The pulp was then dewatered, solvent exchanged with methanol, and air dried at 70°F. and 50% R.H. It was found that this pulp would not readily disperse in water, so it was redispersed with a 30-second Waring Blendor treatment and dewatered to approximately 25% solids content. Pads, about one-inch thick, were then sealed in polyethylene bags and placed in a freezer overnight. The pads were then added to six parts chilled ethanol and the solution kept below 0°C. for 24 hours. After this period, the pulp was removed, pressed slightly, and redispersed in six parts fresh ethanol at room temperature. Twenty-four hours later the pulp was pressed and allowed to air dry at 70°F. and 50% R.H. This yielded a product that was easily dispersed in water. This pulp had an 800-ml. Schopper-Riegler freeness.

PREPARATION OF THE GLUCOMANNAN FOR THE SORPTION STUDY

In sorption experiments, the glucomannan was added to the pulp as an aqueous solution. Approximately 1% solutions of the acetylated glucomannan were made up and they were allowed to rotate overnight at room temperature. The solutions were then filtered through coarse fritted-glass filter funnels and the exact concentrations

*Schopper-Riegler freeness will be reported in terms of ml. of water, rather than beating degree.

determined by colorimetric analysis (see Appendix III). This concentration was also determined by freeze-drying an aliquot in a tared weighing bottle and reweighing after 60°C. vacuum drying. This aliquot corresponded to the amount added to each sorption sample. (Filtering did not affect the measured concentrations.)

Deacetylated glucomannan was prepared by saponifying the acetyl groups with 0.1N sodium hydroxide. Approximately 2% solutions of acetylated glucomannan were allowed to rotate overnight. They were then slowly added to equal volumes of 0.2N sodium hydroxide, stirred for several hours, and brought to a neutral pH with a mixed-bed ion-exchange resin. The deacetylated glucomannan was isolated from the resin by filtering the solutions through coarse fritted-glass filter funnels. Actual concentrations were determined as with the acetylated polymer. Acetyl determinations (Appendix II) indicated that deacetylation was complete and cuene intrinsic viscosity measurements demonstrated that there was no polymer degradation.

Fresh deacetylated glucomannan was prepared prior to each sorption run as these solutions (1%) had a tendency to become quite viscous with time, especially when refrigerated. Once isolated from solution, the deacetylated polymer would not redissolve in water. A time-viscosity study was carried out on samples of both acetylated and deacetylated glucomannan dissolved in water at the concentrations employed during sorption. No appreciable change in viscosity was observed in either case. This indicates that gelling or precipitation of the glucomannan is not a problem in the concentration range used (0.05 to 0.1%).

Samples of intermediate acetyl content were produced by the addition of controlled amounts of sodium hydroxide, but a specific degree of deacetylation or duplicate partial deacetylation could not be produced.

SORPTION STUDIES

SORPTION APPARATUS

All sorption runs were carried out in sealed bottles that were rotated in a constant temperature (25 ± 0.05°C.) bath. Agitation was provided by mounting the bottles between the peripheries of two parallel metal disks, independently mounted on a common shaft. The peripheries of the disks are notched, and disks with notches of different sizes were utilized to accommodate the various bottle types used. Elastic bands were used to secure the bottles to the disks, about five inches from the shaft. The rate of rotation was maintained at 30 r.p.m. Good agitation was obtained by advancing one of the disks a few degrees so that the axes of the sorption bottles were not parallel to the shaft.

SORPTION PROCEDURE

Glucomannan was sorbed onto the cotton-linter substrate in order to examine sorption rates, to observe the molecular character of the polymer sorbed, and to provide sorbed pulp samples for papermaking evaluations. While a different size bottle was used for each of these procedures, the methods of carrying out the sorption were essentially the same. Initial studies were concerned with rate and equilibrium so that 50-ml. bottles were sufficient. Larger (125-ml.) bottles were necessary to isolate enough supernatant material for intrinsic viscosity analyses, and pint bottles were used for preparing the sorbed pulps.

Sorption measurements were made according to a specific procedure. Weighed samples of air-dried cotton-linter pulps were placed into the sorption bottles along with the required amount of distilled water (to obtain a final pulp consistency of approximately 0.8%). The bottles were then sealed and rotated in the bath for 24 hours to facilitate complete pulp dispersion. The desired quantities

(around 10% of the cotton-linter weight) of glucomannan were then pipetted into the sample bottles, which were then resealed and returned to the bath. At specified times, samples were removed and the supernatants isolated by rapidly blowing the suspensions through coarse fritted-glass filter funnels.

Quantities sorbed were determined by measuring changes in the concentration of the supernatant material. These changes were measured both gravimetrically and colorimetrically. The simplest method involved freeze-drying and weighing an aliquot. Supernatant concentrations were also determined colorimetrically by the phenol-sulfuric acid color reaction (34). This method was recently employed by Eriksson, et al. (11) and proved quite satisfactory. Walker (10) found that, when using cotton-linters, any cellulose solubility was within the range of the phenol-sulfuric acid colorimetric measuring error.

A linear relationship has been established (see Appendix III) relating absorbance to glucomannan concentration with a DU Beckman spectrophotometer, at a wavelength of 490 nm.:

$$C = 55.5\ A \qquad (8).$$

C represents the glucomannan concentration in micrograms per ml. and A is the absorbance read. The amount of glucomannan present in the supernatant is determined by correcting C for any sample dilution, multiplying by the sample size, and converting to the desired units. This can be expressed:

$$L = (NCD)/10^3 \qquad (9).$$

N is the total number of ml. comprising the sorption sample; L is the amount of glucomannan not sorbed, expressed in mg.; and D is the dilution of the sample prior to colorimetric analysis. (That is, if it were necessary to dilute 1 ml. of the supernatant material to a total of 20 ml., then D would equal 20.) The amount of

glucomannan sorbed is then determined by subtracting L from the initial quantity of glucomannan added. A blank sample (containing no glucomannan) was analyzed after 124 hours and only negligible amounts of carbohydrate were detected. Sorption results are summarized in Tables XI and XII of Appendix IV.

In order to determine whether the sorption is reversible with respect to concentration and to check the colorimetric method, pulps containing deacetylated and acetylated glucomannan were washed thoroughly and the amount sorbed determined by both quantitative paper chromatography (see Appendix II) and the colorimetric method. These results are shown in Table V.

TABLE V

COMPARISON OF CALCULATED AMOUNT SORBED FOR COLORIMETRIC AND CHROMATOGRAPHIC METHODS

Sample	Specific Sorption, % of cotton linter weight By Colorimetric Method on Supernatant	By Quantitative Chromatography on Pulp
Pulp and acetylated glucomannan	7.21	7.38 ± 0.5
Pulp and deacetylated glucomannan	8.11	8.23 ± 0.5

This comparison indicates both that the glucomannan does not wash off the pulp and that the colorimetric analysis of the supernatant provides a good measure of quantities sorbed.

Quantitative sugar contents were also determined on samples obtained from the supernatant at various times during sorption runs with both acetylated and deacetylated polymer. These results are shown in Table VI.

It appears that there is a slight decrease in both glucose and mannose content of the glucomannan isolated from the supernatant solutions of acetylated glucomannan. It is felt that these decreases are inherent to the experimental procedure

and would not indicate cellulose dissolution. In the case of the deacetylated polymer the amount of both glucose and mannose in the supernatant appears to increase slightly. This may be due in part to the absence of acetyl groups. (That is, no acetyl groups would increase the relative amounts of other constituents.) There may also be a slight amount of cellulose dissolution in the presence of deacetylated polymer, although the supernatant glucose content does not vary with time.

TABLE VI

QUANTITATIVE SUGAR CONTENT OF SAMPLES ISOLATED FROM THE SUPERNATANT OF ACETYLATED AND DEACETYLATED GLUCOMANNAN

	Glucan, %	Mannan, %
Starting material	25.7 ± 0.5	67.7 ± 2.0
Acetylated glucomannan sorption time, hr.		
24	24.5 ± 0.5	62.6 ± 0.5
138	23.3 ± 0.5	60.1 ± 0.5
240	22.5 ± 0.5	61.3 ± 0.5
Deacetylated glucomannan sorption time, hr.		
19	27.5 ± 0.5	68.0 ± 0.5
55	27.2 ± 0.5	68.9 ± 0.5
240	28.0 ± 0.5	65.4 ± 0.5

An experiment was carried out to determine whether phenyl mercuric acetate could be added to the sorption samples in order to insure the absence of biological degradation. It was found (see Appendix V) that this chemical affected the sorption behavior and could not be used. It has been determined, however, that the intrinsic viscosity of the glucomannan does not change after being subjected to sorption conditions for five days in the absence of pulp. The water used to dissolve the glucomannan was isolated from a pulp subjected to sorption conditions for 48 hours.

TREATMENT OF SUPERNATANT MATERIAL

In order to evaluate selective sorption due to molecular weight as well as polymer exchange at the cellulose surface, samples of the supernatant were isolated at various times during sorption runs with both acetylated and deacetylated glucomannans. Intrinsic viscosities were then determined on each sample, and molecular weights were calculated with equations which relate number average molecular weight to intrinsic viscosity. While the intrinsic viscosities of the acetylated glucomannan were determined in 1.0% sodium chloride, cuene had to be used for the water-insoluble glucomannan. Results of the intrinsic viscosity measurements and the corresponding molecular weights are summarized in Table XIV of Appendix IV.

GLUCOMANNAN COTTON-LINTER PULP PREPARATION

Pulps were produced with similar amounts of sorbed acetylated and deacetylated glucomannan, so that the effects of glucomannan acetyl content on papermaking properties could be evaluated. This was accomplished by varying sorption time and amounts of polymer added.

A British disintegrator was used to disperse approximately 60 grams of the cotton-linter pulp. The pulp was diluted to eight liters and 400-ml. portions were added to each of twelve pint Mason jars. A portion (2400 ml.) was dewatered and refrigerated for use as the unsorbed control pulp. The jars were sealed and rotated for 24 hours, after which the desired quantities of acetylated and deacetylated glucomannan were added. At the conclusion of the sorption period, the pulps were filtered, washed thoroughly with distilled water, and dewatered. Sorption conditions and some properties are listed in Table VII.

TABLE VII

CONDITIONS AND RESULTS OF SORPTION OF BOTH ACETYLATED AND DEACETYLATED GLUCOMANNAN ONTO COTTON LINTERS

Property	Deacetylated	Acetylated Glucomannan
Pulp consistency, %	0.786	0.786
Glucomannan added, % of cotton linter weight	9.07	12.48
Specific sorption, % of cotton linter weight	7.43	7.23
Time, hr.	18	53

REFINING PROCEDURE AND PAPER EVALUATION

The three pulps (cotton-linter control pulp, acetylated-glucomannan pulp, and deacetylated-glucomannan pulp) were refined by a modified procedure, utilizing a Jokro mill. Because of the small size (approximately 16 g.) of each pulp sample, continuous refining was employed and freeness samples were reclaimed. The step-by-step beating procedure is listed in Appendix VI.

Four handsheets were prepared for each pulp at each beating interval (0, 15, and 30 minutes) according to Institute Method 411. Strength tests were performed according to standard procedures. Tensile strengths were measured using one-inch wide strips on the Instron instrument with a four-inch span.

Quantitative paper chromatography was used to determine the mannose content of the handsheets. The sheets containing acetylated glucomannan had 5.6, 5.7, and 5.2% mannose for the 0, 15, and 30-minute refining times; while the sheets containing deacetylated polymer had 5.0, 5.3 and 5.3% mannose content for the same intervals. These results indicate that the mannose contents of the sheets were approximately the same and little or no glucomannan was lost during refining and sheet making. There was no mannose found in the sheets made from the cotton-linter control pulp.

RESULTS

SORPTION STUDIES

PRELIMINARY RESULTS

Preliminary sorption experimentation was concerned with examining system variables such as pulp consistency, quantity of glucomannan addition, and time of sorption. Some results from these investigations are presented in Table VIII.

TABLE VIII

EFFECT OF SYSTEM VARIABLES ON ACETYLATED GLUCOMANNAN SORPTION

Sample	Pulp Consistency, %	Sorption Time, hr.	Glucomannan Added, % of cotton linter weight	Specific Sorption, % of cotton linter weight
A-1	0.407	96	6.95	4.59
A-2	0.0463	96	61.20	10.25
A-3	0.693	96	4.12	3.87
A-4	1.098	144	4.93	4.50
B-1	0.622	42	3.24	3.10
B-2	0.648	42	3.13	3.05
B-3	0.625	42	3.22	3.05
B-4	0.607	42	3.32	3.12
B-5	0.647	69	3.15	3.06
B-6	0.593	69	3.39	3.25
B-7	0.607	69	3.32	3.12
B-8	0.647	69	3.11	3.09

These experiments indicated that specific sorption (amount of glucomannan sorbed, expressed as percentage of cotton-linter pulp weight) increases with decreasing consistency and increasing polymer addition over the ranges studied. Samples A-1, A-2, and A-3 differed only in the amount of pulp present. These experiments also indicate (Samples B-1 to B-8) that the sorption measurements are quite reproducible and that a sorption mass equilibrium occurs with time. Preliminary investigations assisted in determining the sorption conditions for studying the effect of acetyl content on sorption.

EFFECT OF ACETYL CONTENT ON SORPTION BEHAVIOR

The effect of acetyl content on glucomannan sorption was evaluated by establishing rate curves at similar pulp consistencies and glucomannan additions. The only variable was acetyl content. In general, only acetylated and completely deacetylated glucomannan were evaluated. However, two sorption runs were carried out using partially deacetylated glucomannan.

Figure 3 illustrates the sorption rate curves for acetylated, partially deacetylated, and deacetylated glucomannan at a pulp consistency of 0.68% and an approximate glucomannan addition of 10% of the cotton linter weight. (These and subsequent rate curves are constructed from data located in Appendix IV.) These rate curves indicate that the removal of glucomannan acetyl groups leads to both a higher initial rate of sorption and a larger specific sorption at mass equilibrium. Mass equilibrium was reached after approximately 20 hours with the deacetylated glucomannan, but approximately 50 hours were required with the acetylated glucomannan.

It was found that the rate curves for partially deacetylated glucomannan lie between those for the acetylated and deacetylated glucomannans. The rate curves for the two partially deacetylated glucomannans were quite close, being almost coincidental. The curve representing glucomannan of lower acetyl content appears

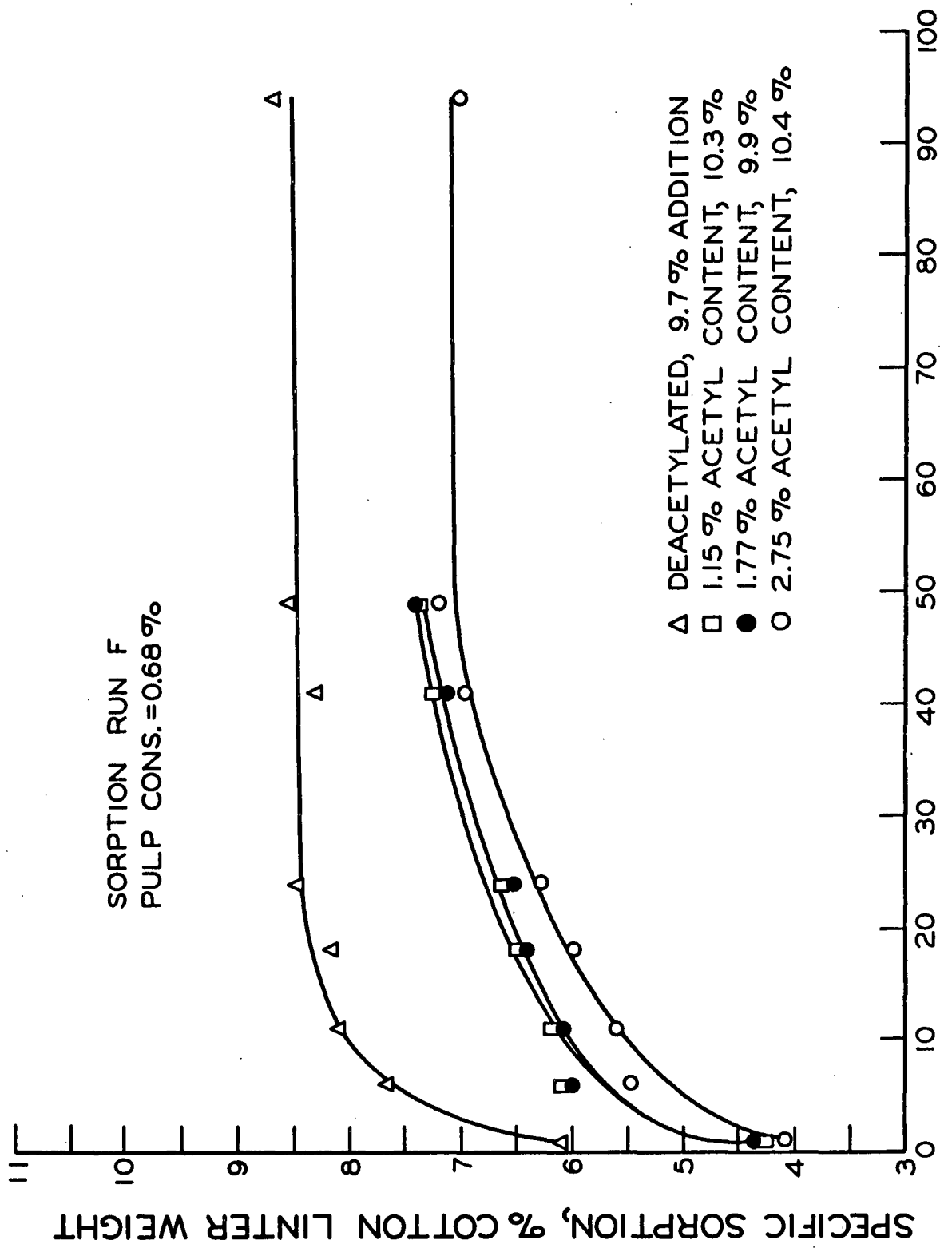

Figure 3. Comparison of Sorption Rates for Acetylated, Deacetylated, and Partially Deacetylated Glucomannan

to be slightly above the other. It should be observed that both of the partially deacetylated glucomannan rate curves are much closer to the rate curve for the acetylated glucomannan. This indicates that only a small amount of acetylation is necessary to provide a marked difference in the glucomannan sorption behavior. It appears that once this low degree of acetylation is present, additional acetylation does not appreciably affect the rate curves.

Figures 4 and 5 compare the rates of sorption for acetylated and deacetylated glucomannan at two different levels of glucomannan addition. At 10% glucomannan addition, the deacetylated glucomannan reaches a mass equilibrium specific sorption of 8.1% after about 25 hours while the acetylated glucomannan reaches a mass equilibrium of 7.1% after 50 hours. When the glucomannan addition is increased to 14.5%, these figures go to 11.5% and 20 hours for the deacetylated glucomannan and 7.4% and 40 hours for the acetylated one. In going from 10 to 15% glucomannan addition, the equilibrium amount sorbed increases proportionately with the deacetylated glucomannan but not appreciably with the acetylated glucomannan. The acetylated glucomannan did appear to reach a mass equilibrium earlier at the higher concentration. These results indicate that, over the range studied, there is a maximum amount of acetylated glucomannan which is sorbed while the amount of deacetylated glucomannan sorbed increases with increasing addition.

Figures 6 and 7 compare rate curves for the additions of different amounts of deacetylated and acetylated glucomannan, respectively. In Fig. 6 it can be seen that increasing additions of deacetylated glucomannan shift the rate curve upward on the specific sorption axis. Figure 7 illustrates that sorption additions of 9 to 15% acetylated glucomannan lead to approximately the same sorption rate curve.

A study was carried out to relate the amount of deacetylated glucomannan sorbed to the amount added. Varying amounts of deacetylated glucomannan were

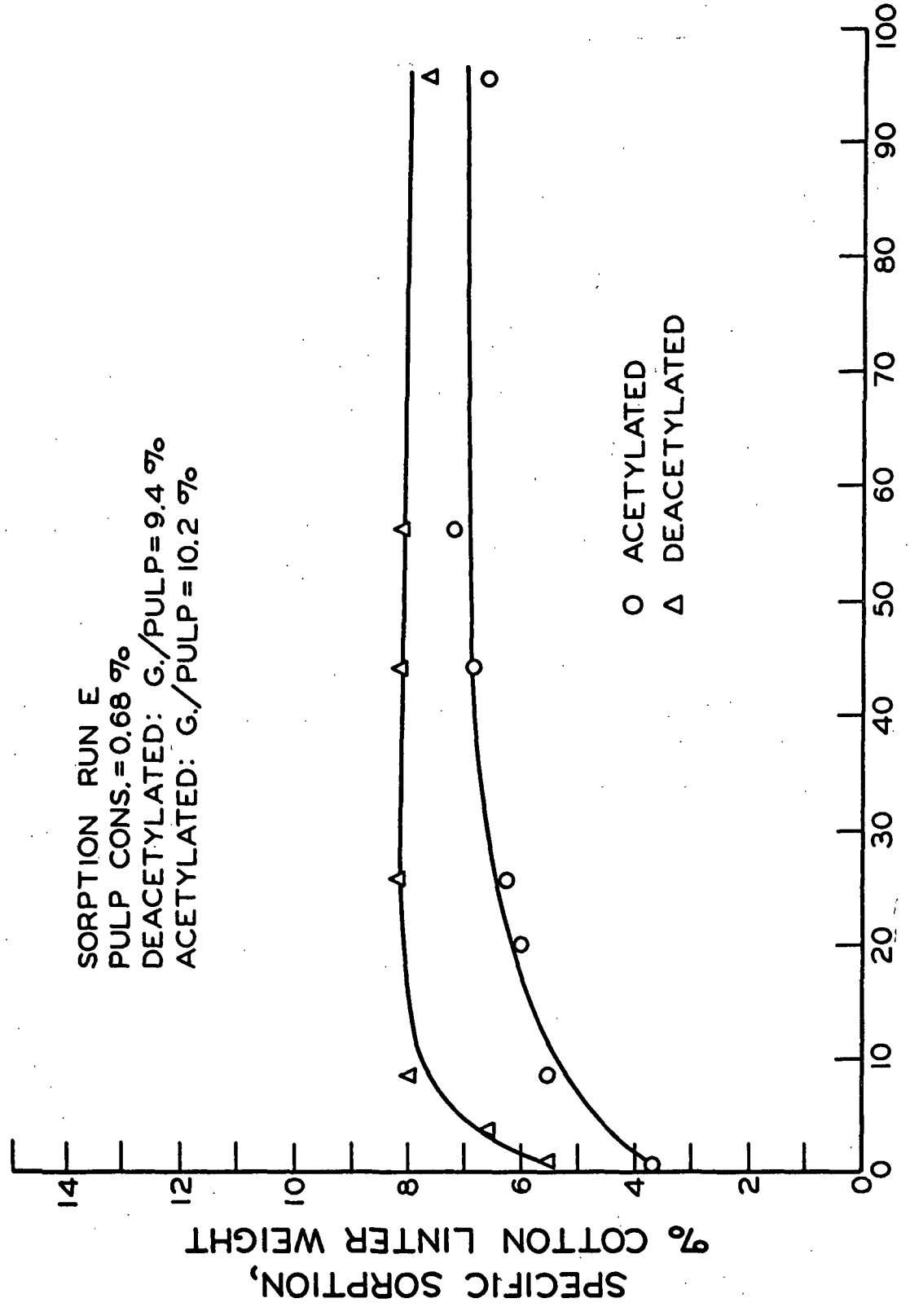

Figure 4. Comparison of Sorption Rates for Acetylated and Deacetylated Glucomannan at 10% Addition

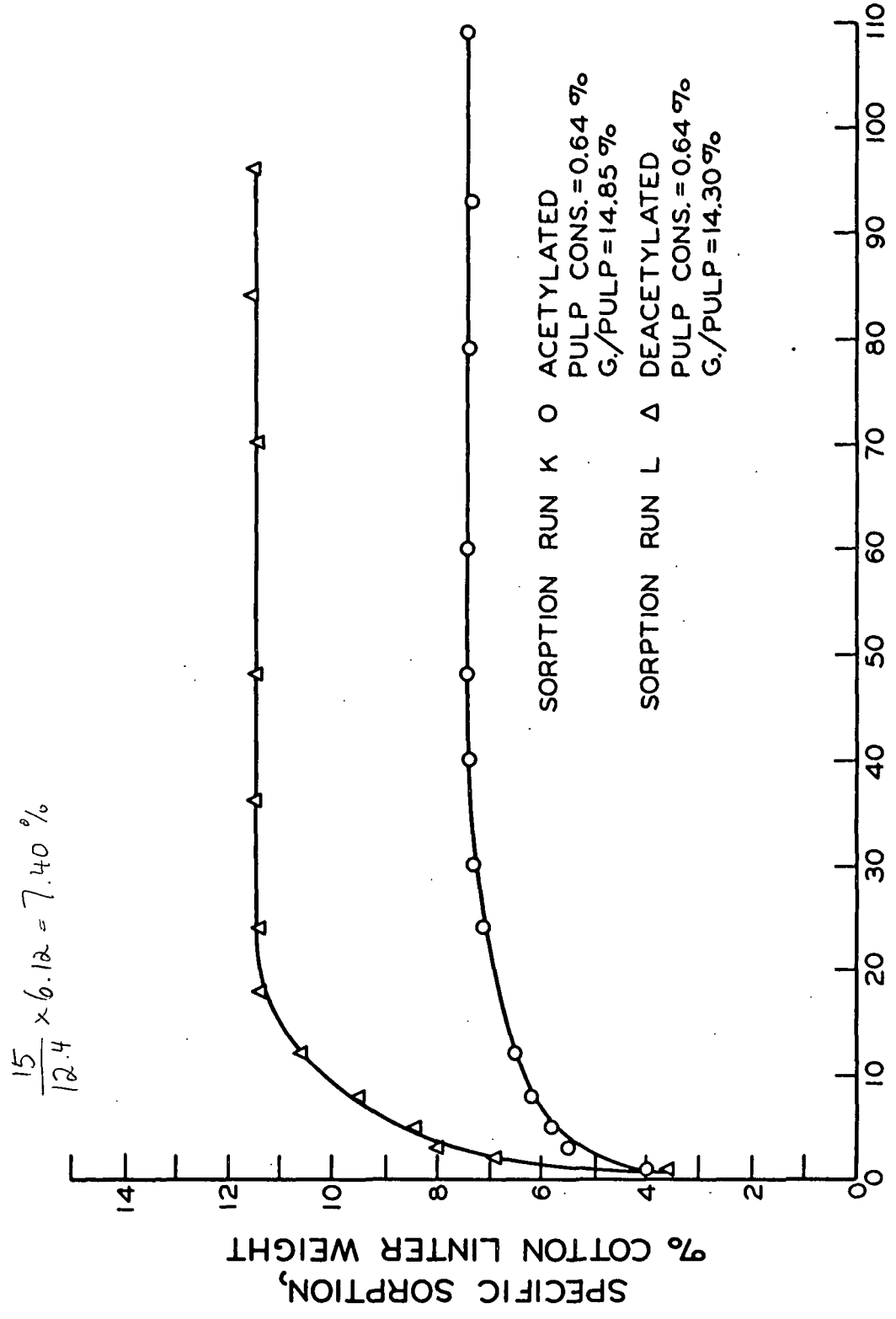

Figure 5. Comparison of Sorption Rates for Acetylated and Deacetylated Glucomannan at 15% Addition

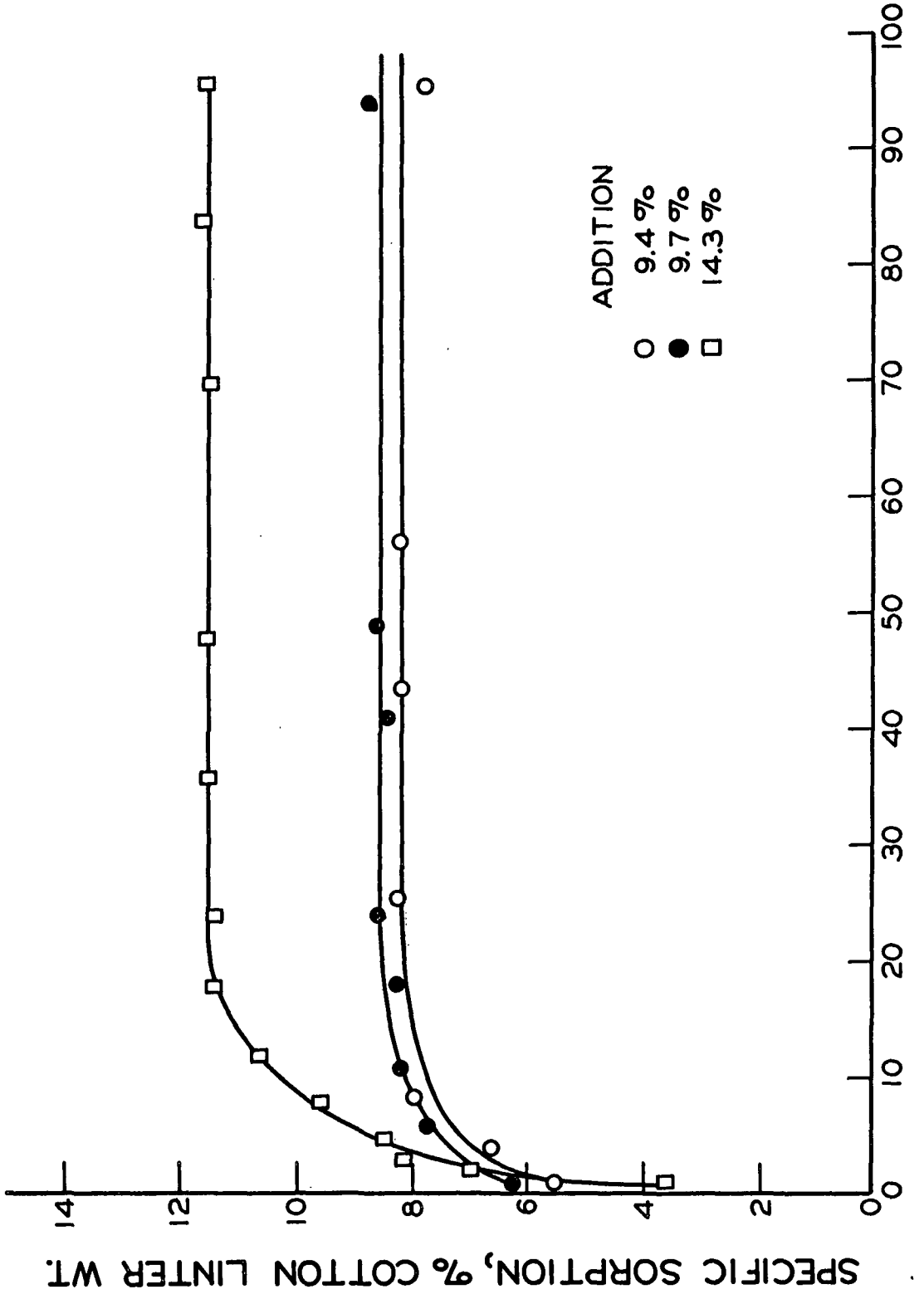

Figure 6. Composite Rate Curves for Deacetylated Glucomannan

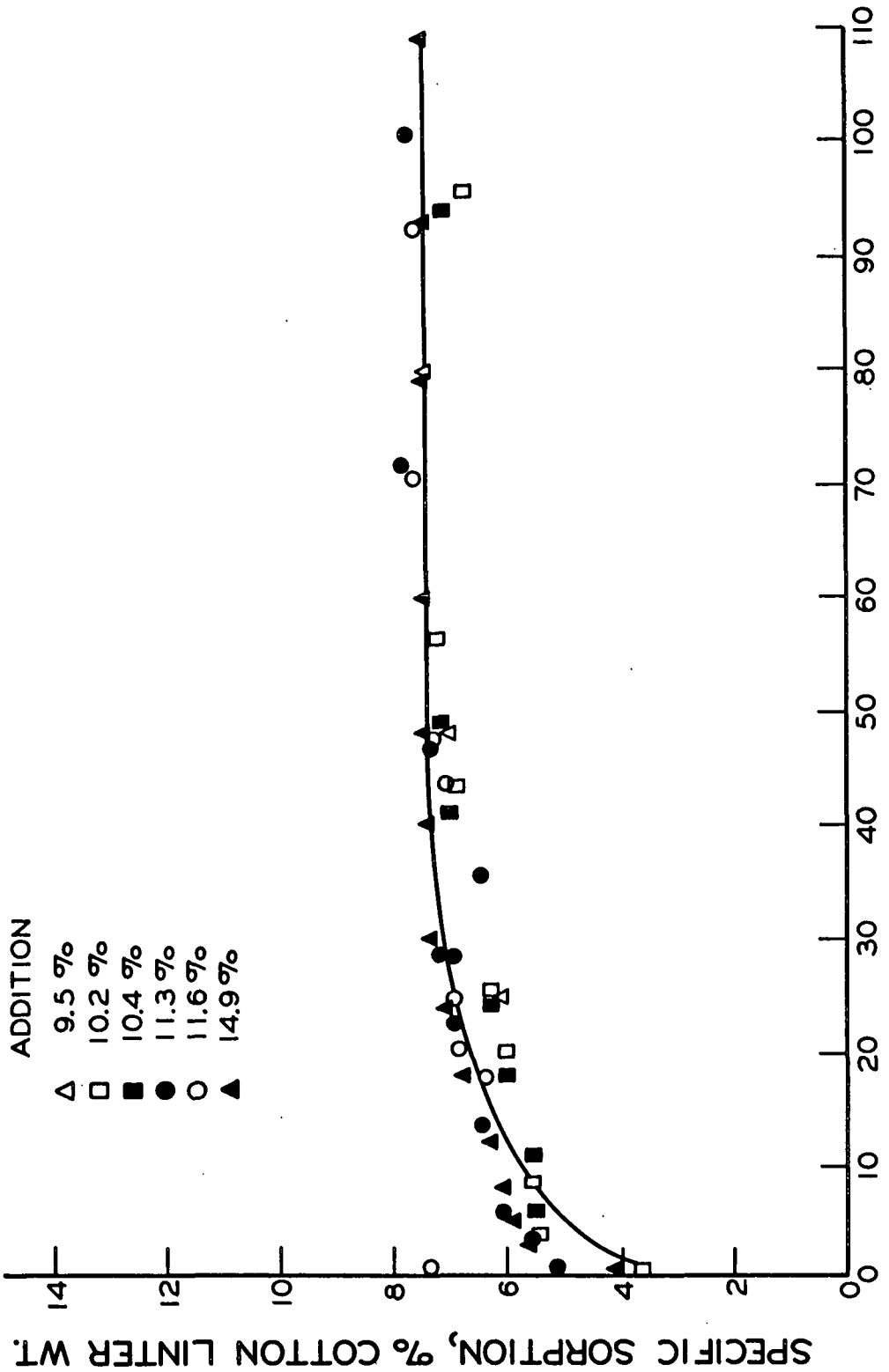

Figure 7. Composite Rate Curve for Acetylated Glucomannan

added to pulp samples and isolated after 24 hours. The results are listed in Appendix IV, Table XIII, and illustrated in Fig. 8. Over the range of glucomannan addition studied, no leveling of the equilibrium amount sorbed was observed.

SELECTIVE SORPTION DUE TO ACETYL CONTENT

Acetyl contents were determined on the glucomannan starting material and that remaining unsorbed in order to determine whether sorption was selective due to the presence of acetyl groups. A sample representing the unsorbed polymer was obtained by combining samples isolated from the supernatant of several sorption runs utilizing acetylated glucomannan. The small amount available (0.5 g.) necessitated modifying the acetyl determination method (see Appendix II). The sample had an acetyl content of 2.775% which compared favorably with the values of 2.732 and 2.738% determined concurrently on acetylated glucomannan. This indicates that the sorption of acetylated glucomannan is not selective due to acetyl content. It should be restated here that the original glucomannan starting material had a uniform acetyl content and selective sorption due to acetyl content would not, therefore, be anticipated.

SELECTIVE SORPTION DUE TO MOLECULAR WEIGHT

Intrinsic viscosities were determined on samples of glucomannan isolated (by freeze-drying) from the supernatant solutions at intervals during sorption runs with both acetylated and deacetylated glucomannan. The solvents for the acetylated and deacetylated glucomannan were 1.0% sodium chloride and cuene, respectively (see Appendix II). Because the viscosities of the bulk and surface phases are additive, the intrinsic viscosities of the material sorbed can be calculated by the equation

$$[\eta]_s = ([\eta]_o - W_B[\eta]_B/W_s \qquad (10)$$

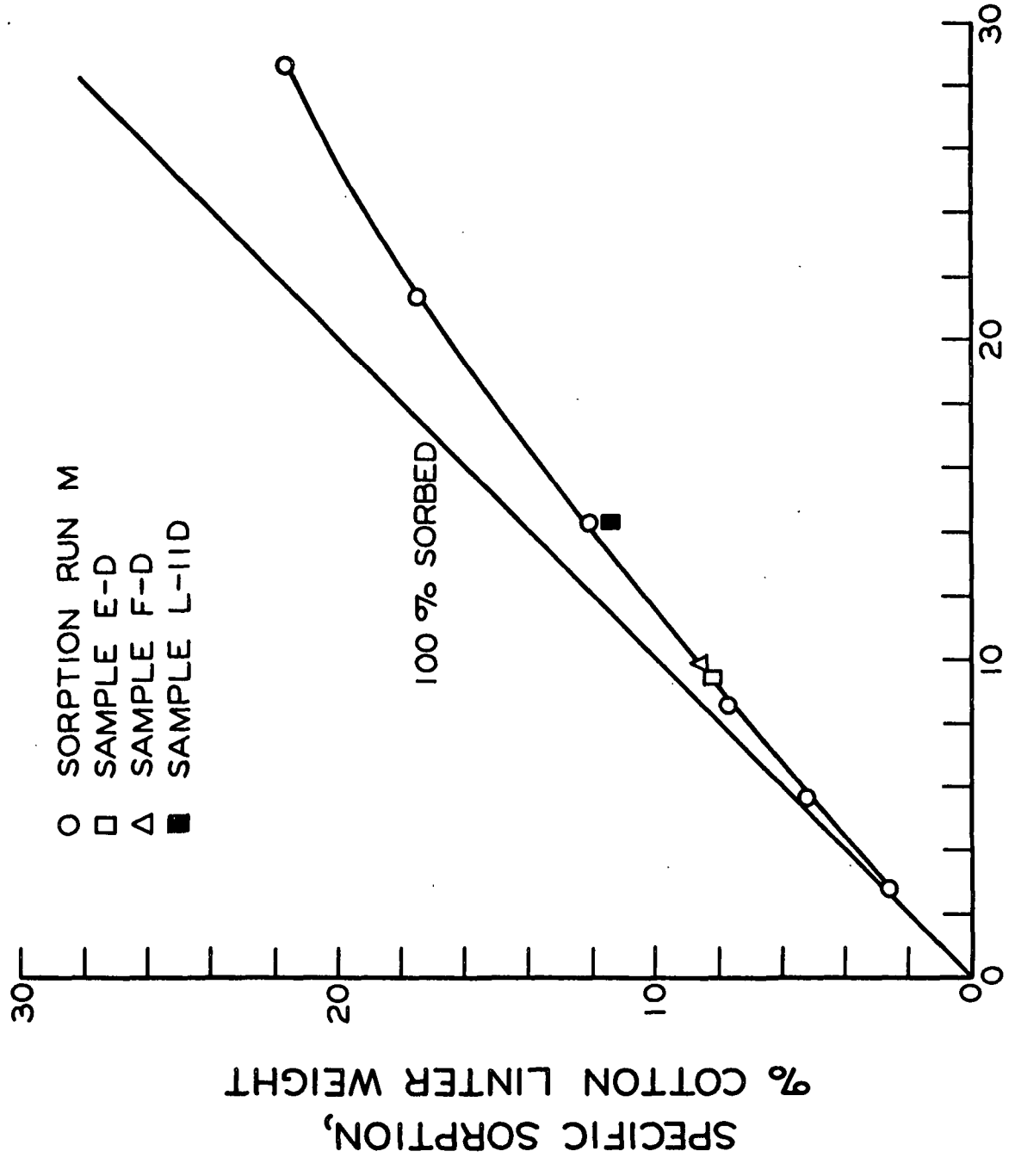

Figure 8. Equilibrium Amounts of Deacetylated Glucomannan Sorbed as a Function of Amount Added

where

$[\eta]_{\underline{s}}$ = intrinsic viscosity of surface polymer

$[\eta]_{o}$ = intrinsic viscosity of starting polymer

$[\eta]_{\underline{B}}$ = intrinsic viscosity of bulk polymer

$\underline{W_B}$ = weight fraction of polymer in bulk phase

$\underline{W_s}$ = weight fraction of polymer in surface phase

Knowing the intrinsic viscosities for both phases, Equations (2) and (3) were utilized to calculate molecular weights of surface and bulk glucomannans. Table XIV of Appendix IV contains intrinsic viscosity and molecular weight values for both surface and bulk polymers at time intervals during acetylated and deacetylated glucomannan sorption runs. Rate curves for these sorption runs have been presented in Fig. 5.

From Fig. 9, it is apparent that lower weight acetylated glucomannan sorbs onto the pulp initially and is slowly replaced by higher weight material. It is of interest to note that, after 40 hours, the mass of polymer sorbed is constant but larger molecules continue to replace smaller ones. Even after five days the viscosity continues to change, although not as rapidly as the semilog plot may appear to indicate.

In the case of deacetylated glucomannan (Fig. 10), the intrinsic viscosity of the bulk phase glucomannan increases gradually for 20 to 30 hours. The viscosity of the bulk phase then remains fairly constant. This leveling of the bulk phase intrinsic viscosity coincides with mass equilibrium. These results support a sorption mechanism for the deacetylated glucomannan in which lower molecular weight material is selectively sorbed initially and in which little or no exchange occurs on the cellulose surface.

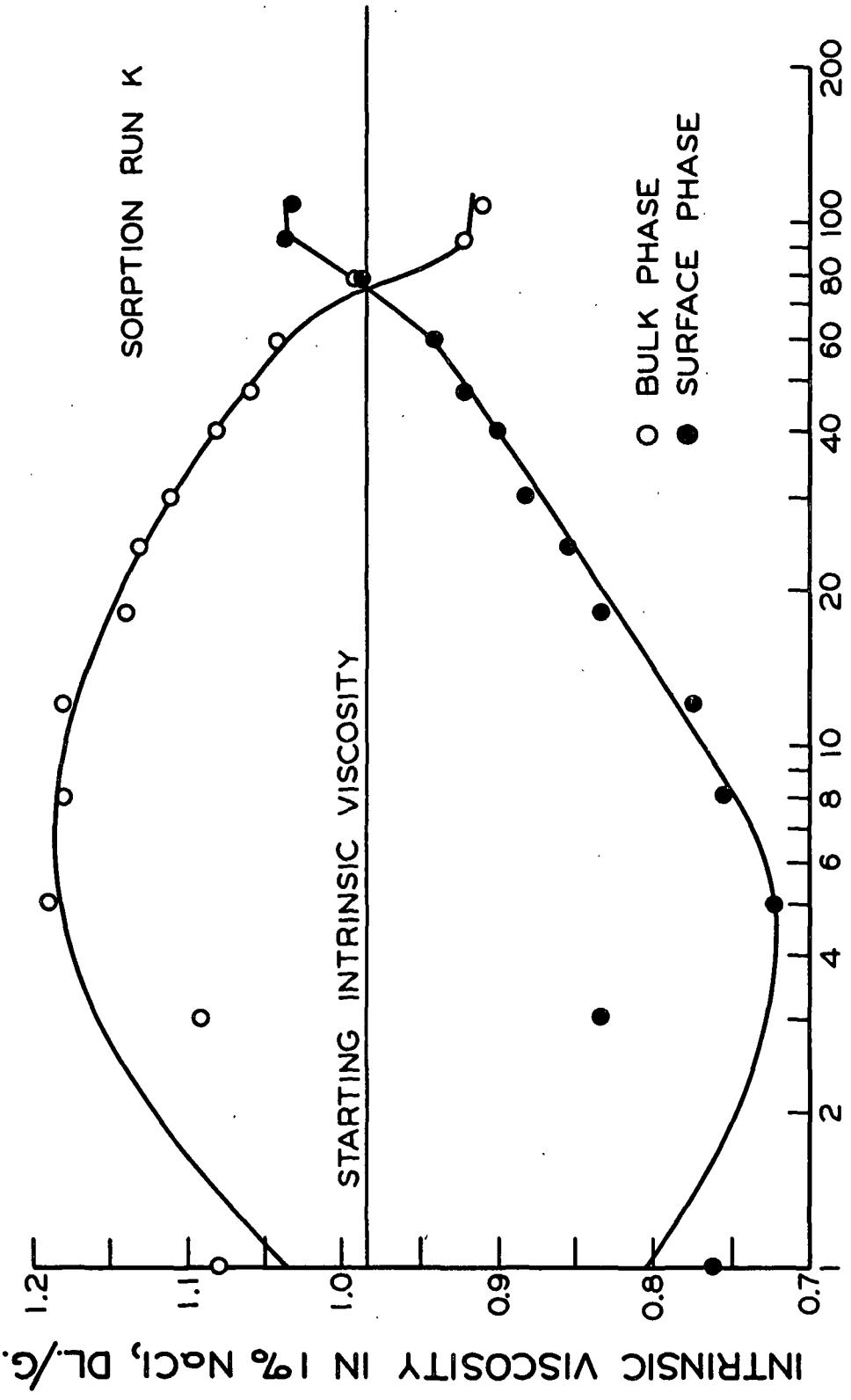

Figure 9. Intrinsic Viscosity of Bulk and Surface Phase Acetylated Glucomannan as a Function of Time

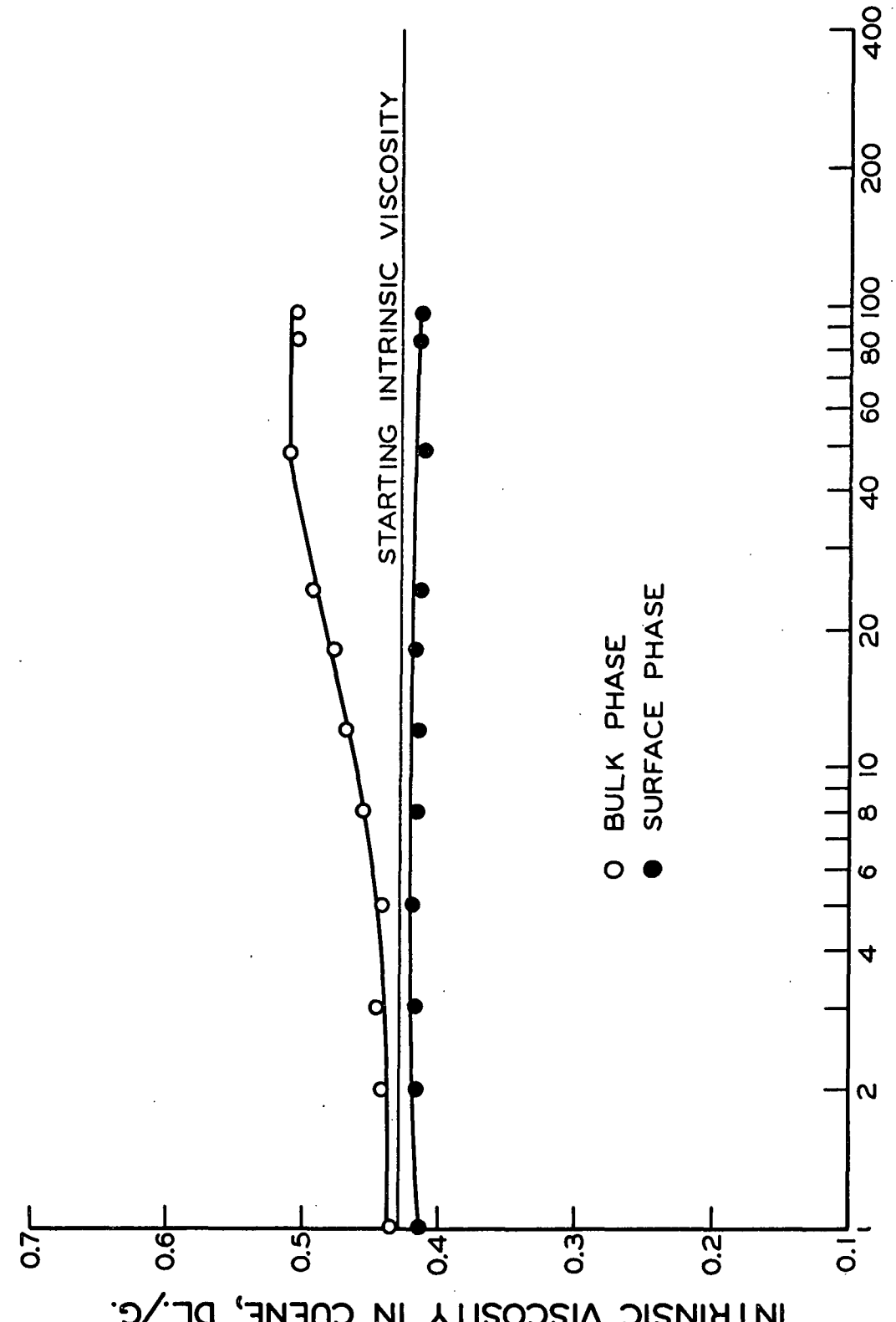

Figure 10. Intrinsic Viscosity of Bulk and Surface Phases Deacetylated Glucomannan as a Function of Time

Figure 11 presents number average molecular weight data for the bulk and surface phases of both acetylated and deacetylated glucomannan. It should be mentioned that while the glucomannan added is approximately the same for each sorption run, a much higher percentage of the deacetylated glucomannan is sorbed. These data afford the same conclusions reached from the viscosity data, but also support the conclusion that exchange may occur with the deacetylated polymer. This exchange, if present, is much less pronounced and considerably slower than that experienced with the acetylated polymer.

REFINING AND PAPERMAKING PROPERTIES

As described in the Experimental section of this thesis, three pulps (cotton-linter control, cotton linters plus acetylated glucomannan, and cotton linters plus deacetylated glucomannan) were refined, and handsheet properties were measured on samples of 0, 15, and 30-minute refining times. The acetylated-glucomannan pulp contained 6.73% glucomannan with an estimated number average molecular weight of 14,540 g./mole. The deacetylated-glucomannan pulp contained 6.91% glucomannan which had an estimated molecular weight of 15,938. (It should be noted that the percentage glucomannan listed here is based on linters plus glucomannan, not cotton linters alone, as previously used to denote specific sorption.) Molecular weights were calculated from bulk phase intrinsic viscosity data.

The results of refining and handsheet testing are summarized in Table XV of Appendix IV. Figure 12 illustrates how freeness of the three pulps decreases with beating time. It appears that the three pulps beat at about the same rate, as the slopes of the three curves are quite similar.

Physical properties of the handsheets are compared in Fig. 13 to 16. The pulps containing the sorbed hemicelluloses had considerably better strength

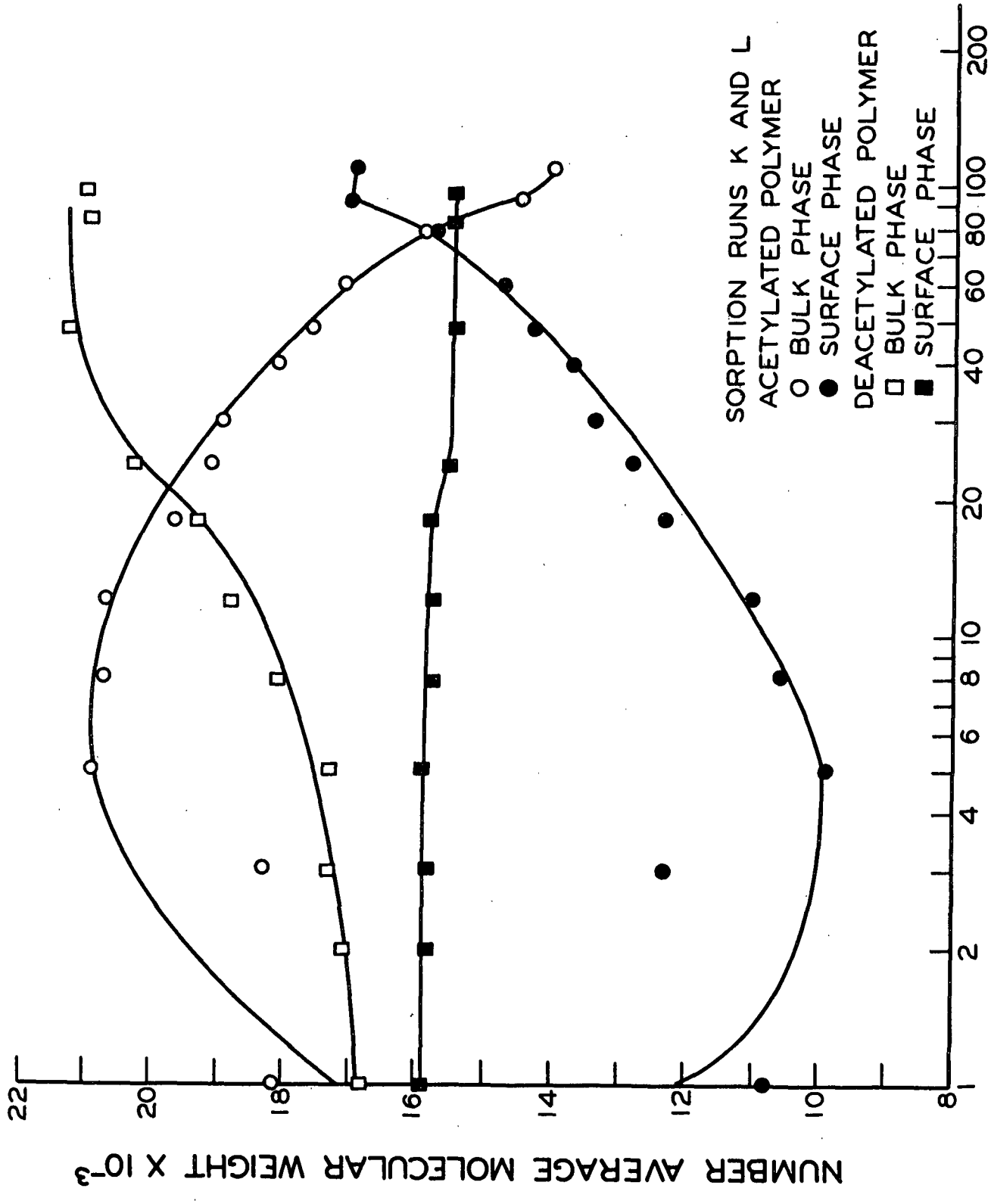

Figure 11. Molecular Weight of Bulk Phase and Surface Phase as a Function of Time

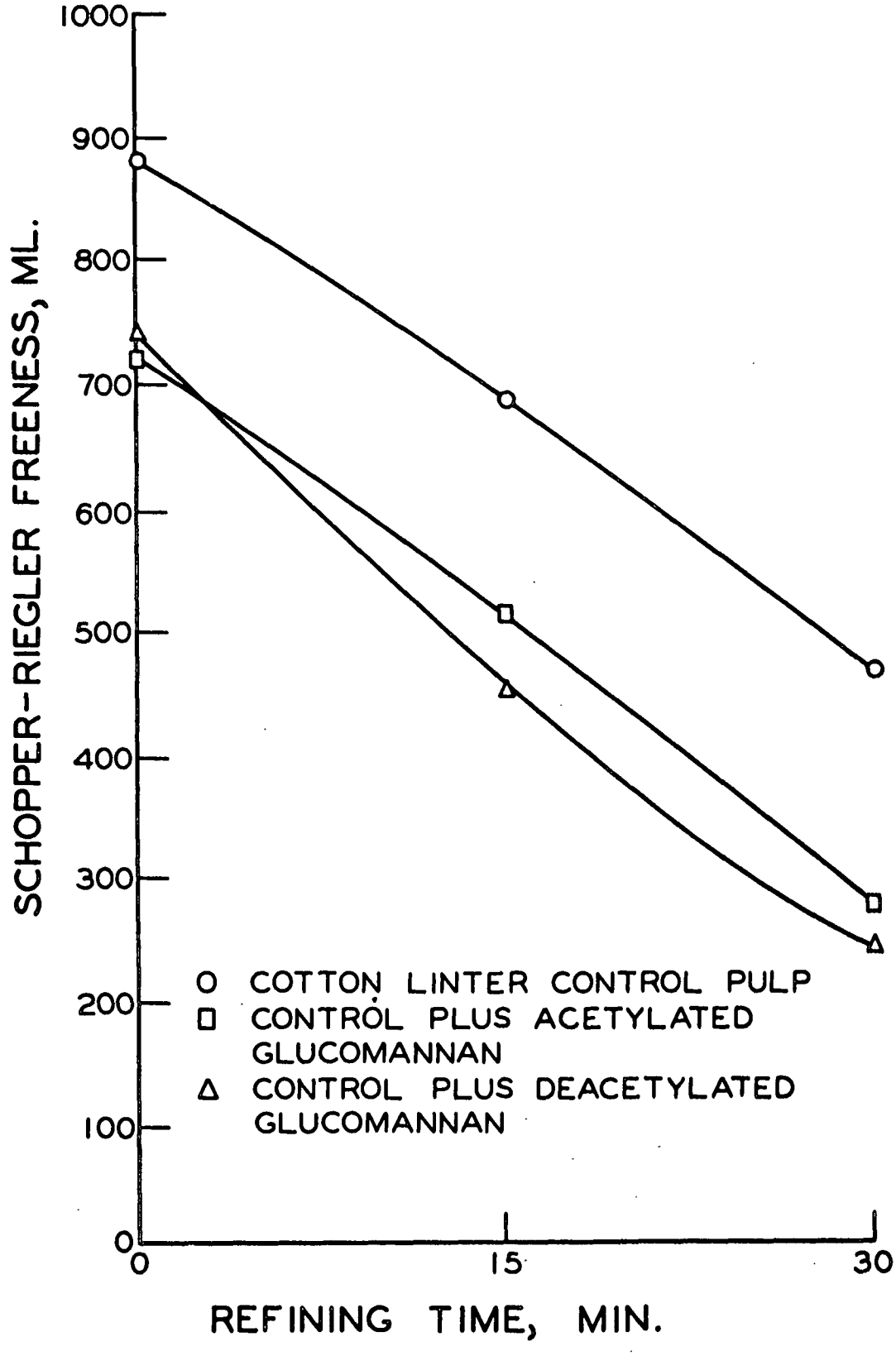

Figure 12. Freeness Versus Refining Time

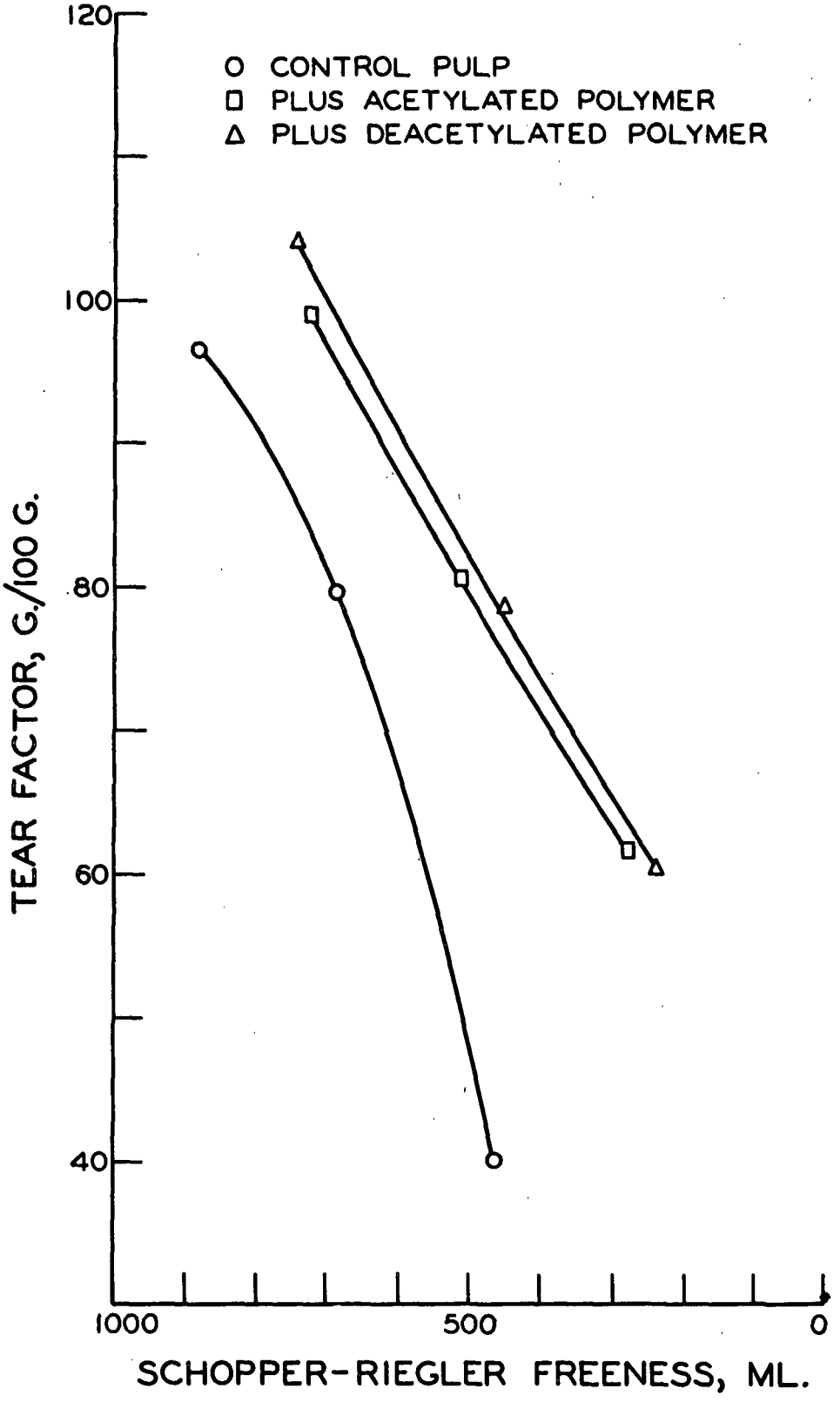

Figure 13. Tear Factor Versus Freeness

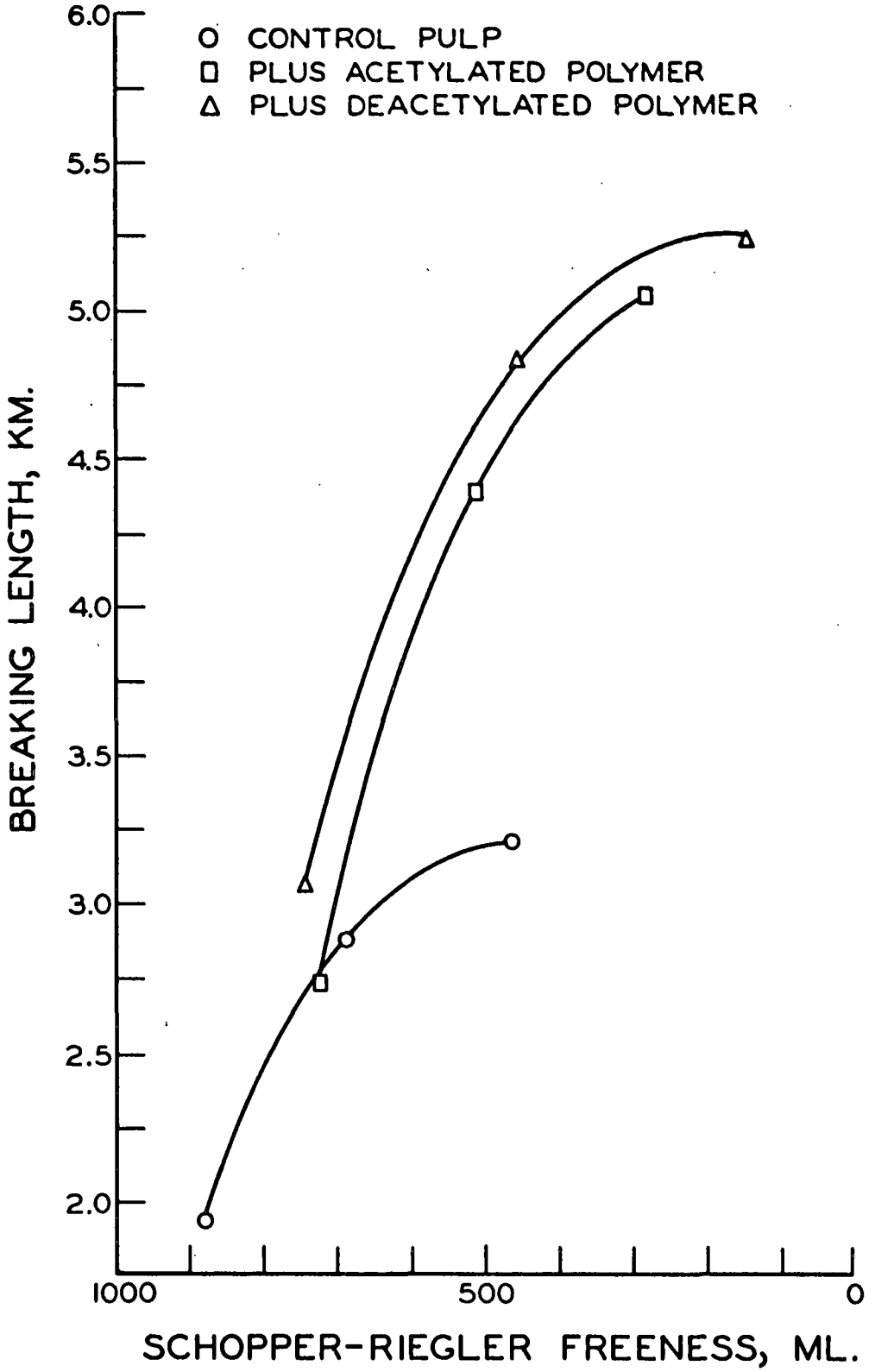

Figure 14. Breaking Length Versus Freeness

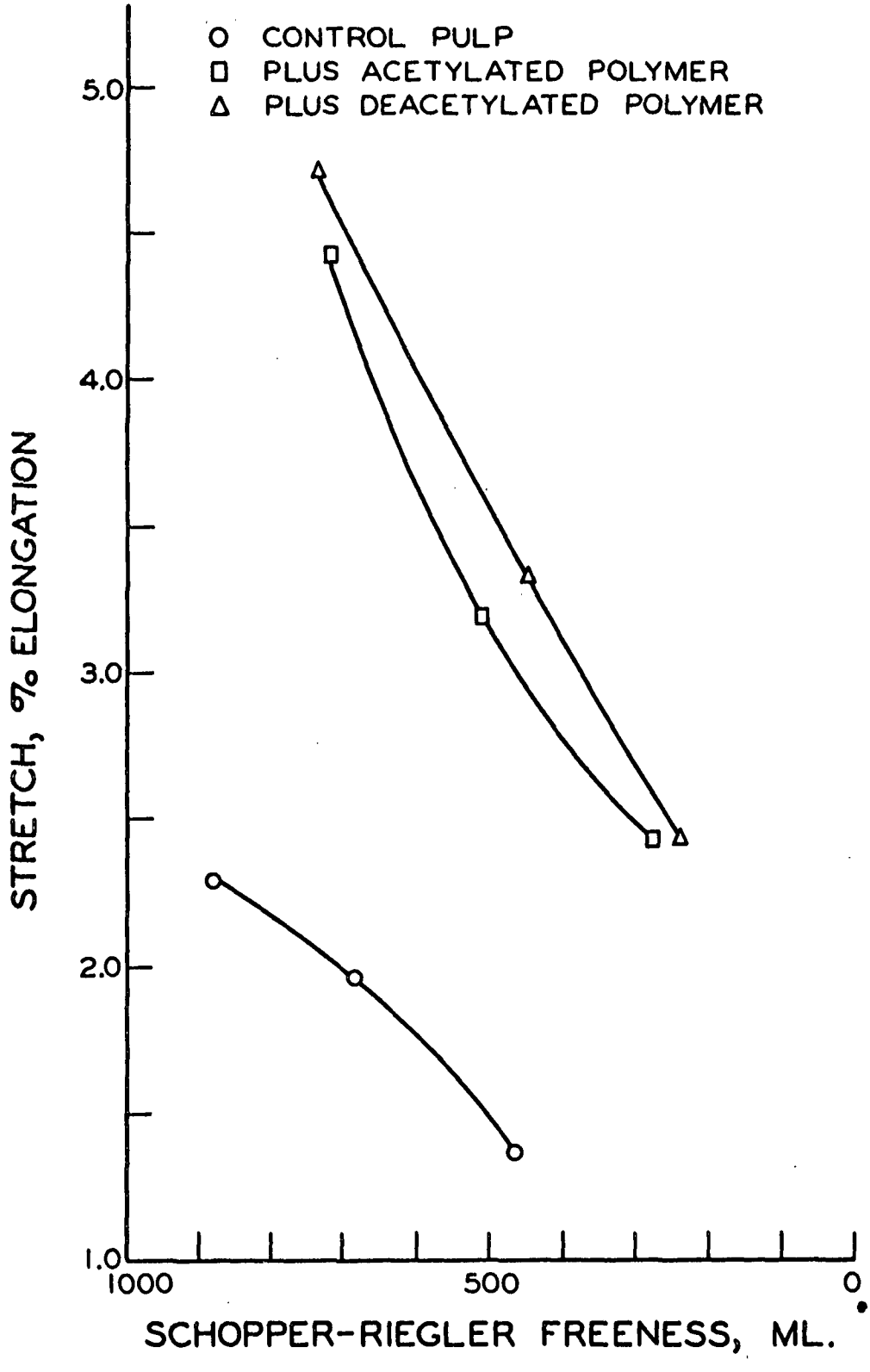

Figure 15. Stretch Versus Freeness

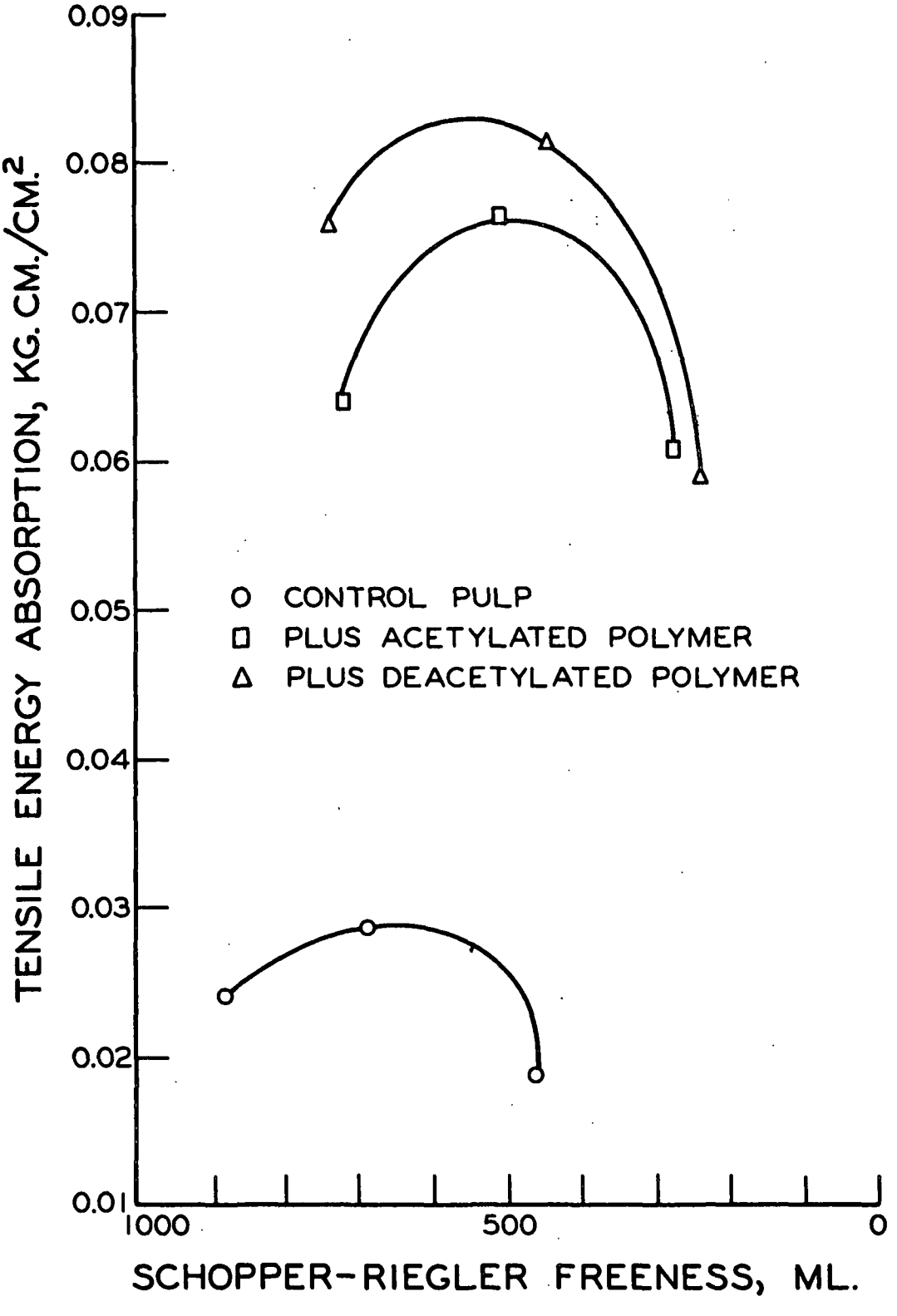

Figure 16. Tensile Energy Absorption Versus Freeness

properties than the cotton-linter control pulp. The handsheets containing the deacetylated glucomannan had higher tear factors, breaking lengths, stretch values, and tensile energy absorption values than the handsheets containing acetylated glucomannan over the freeness range evaluated.

DISCUSSION

EFFECT OF ACETYL SUBSTITUTION ON SORPTION

The results obtained in the sorption study indicate that the presence of acetyl groups greatly influences the sorption behavior of this hemicellulose. It was found that removal of the glucomannan acetyls leads to decreased solubility in water, higher sorption rates, and higher equilibrium amounts sorbed at given levels of glucomannan addition. While the cotton linters would take up, at equilibrium, almost as much of the deacetylated polymer as was added, the equilibrium specific sorption of the acetylated glucomannan approached a limit of slightly over 7% (within the range of addition studied).

Intrinsic viscosity studies on the bulk phase at various sorption times indicate that, in both cases, smaller molecules are sorbed initially. In the case of the acetylated polymer, the viscosity of the bulk phases continues to decrease for several days after mass equilibrium while larger molecules exchange with the smaller molecules on the surface. This effect is not as obvious with the deacetylated polymer. If exchange does occur, it does so at a rate which is much slower than in the case of the acetylated glucomannan. The results of these sorption experiments can be used to construct a qualitative mechanism for glucomannan sorption.

Molecular forces at the surface of a solid are in a state of unbalance or unsaturation. As a result of this unbalance, solid surfaces tend to satisfy their residual forces by attracting onto, and retaining on their surfaces, gases or dissolved substances with which they come into contact. The cotton-linter sorbent used in this study represents such a solid. The surface of this substrate is composed of cellulose molecules which contain hydroxyl groups capable of hydrogen bonding with any suitable solute.

In the system composed of a cotton-linter sorbent dispersed in a solution of aqueous glucomannan, there is a competition between the solvent and the cellulose surface for the glucomannan molecules. The equilibrium distribution of glucomannan between surface and bulk phases is dictated by the partition leading to the maximum decrease in free energy of the system. The equilibrium fraction of material sorbed would be greater in a poorer solvent.

Experimental results support a sorption mechanism in which glucomannan molecules diffuse to the cellulose surface and continue to sorb there until the competition between the surface and solution phases is satisfied. As the smaller molecules diffuse faster, there is an initial selective sorption of low molecular weight material. Thermodynamic considerations would favor the sorption of high molecular weight material due to its lower solubility and greater stability on the cellulose surface. It is, therefore, expected that higher weight glucomannan would replace lower weight material. The degree and rate of this exchange would be directly related to the tenacity with which the molecules are held on the surface.

The acetyl groups are quite bulky and prevent the glucomannan from crystallizing. Because the amount sorbed approaches a limit, it is hypothesized that monolayer* sorption occurs with the acetylated glucomannan. (It is of interest to note that by assuming a surface area of 100 $m.^2/g.$ for the cellulose, a monomer size of 35 $A.^2$, and that one-third of the molecules are actually on the surface, a specific sorption of 5.7% is calculated for a monolayer. For the system involved, this type of calculation is, at best, quite inaccurate.) This monolayer would be made up of glucomannan

*In a strict sense, a monolayer would be only one molecule thick. In this discussion the term is used to indicate that the glucomannan only sorbs onto cellulose and not previously sorbed glucomannan. Looping of the polymer might lead to sorbed films many monomer units thick.

molecules with only a portion of each chain actually hydrogen bonded to the cellulose surface and the remainder looped or free in the solution. It is also anticipated that this layer is somewhat of an intermediate stage between undissolved and dissolved material and it is in a semisolid, or gel, state.

The deacetylated polymer acts quite differently. As the amount sorbed does not approach a limit, multilayer sorption must be occurring. In the case of the deacetylated polymer, it is felt that the unsaturation of the surface is not changed after a molecule sorbs onto it. Instead of providing a transition state, the sorbed area provides another unsatisfied surface. This would be due to the high degree of order attained by the sorbed polymer and its poor solubility in the solvent. This would catalyze removal of much of the polymer from solution and lead to multilayer sorption. Experimental results indicate that little or no polymer exchange occurs with the deacetylated polymer.

POLYMER EXCHANGE

Polymer exchange is related to the ease with which a molecule in solution can replace a smaller one on the surface. If the surface bonding is considered to be dynamic (that is, a continual breaking and reforming of hydrogen bonds), exchange can be visualized as larger molecules gradually taking over the sites of smaller molecules and eventually freeing them into solution. Although the sorption of higher molecular weight material is thermodynamically preferred, the rate and degree of exchange is related to the tenacity of polymer-sorbent association. While hydrogen bonding is a special form of physical (van der Waals) sorption, the polymer is probably more tightly bound by hydrogen bonding than with other physical sorption. Emery (31) examined the exchange phenomenon for a system in which polystyrene was sorbed onto graphitized carbon black in 1,2-dichlorethane and found that the viscosity of the supernatant material leveled off after about three days, indicating

completion of polymer exchange. This system has only simple physical sorption which is characterized by very low heats of adsorption. Kindler and Swanson (40) have recently carried out a similar study of the sorption of polyethylenimine onto alpha-cellulose pulp. This system has simple physical sorption plus ionic attraction between secondary nitrogen atoms on the polymer and carboxyl groups present in the pulp. The heat of adsorption here would be higher than that in Emery's system. The glucomannan-cellulose systems examined by this writer are characterized by hydrogen bonding and have still higher heats of sorption.

Figure 17 presents supernatant viscosity as a function of time for Emery's polystyrene-graphitized carbon black system, Kindler's polyethylenimine-cellulose system, and this writer's glucomannan-cellulose systems. The viscosity axis is not the same for each plot. For each sample the starting intrinsic viscosity is shown and the viscosity axis is marked off in units of 0.1 dl./g. The only exception is that each unit is equal to 0.05 dl./g. for the deacetylated glucomannan plot.

This figure indicates that the four systems seem to follow very similar paths, but are out of phase with respect to time. Emery's system with only simple physical sorption reaches an equilibrium viscosity after about three days. Kindler's system with ionic sorption is beginning to level out after four days but has not reached equilibrium. The acetylated glucomannan, characterized by monolayer hydrogen bonding, has not leveled out after five days, and the deacetylated glucomannan system shows no evidence of a decline at all. This comparison indicates that while exchange may occur in all systems, the rate of exchange is directly related to the tenacity of the polymer-sorbent interaction. In this interpretation other system variables such as solubility, molecular size, and concentrations have not been considered, but the relationship shown seems quite prominent.

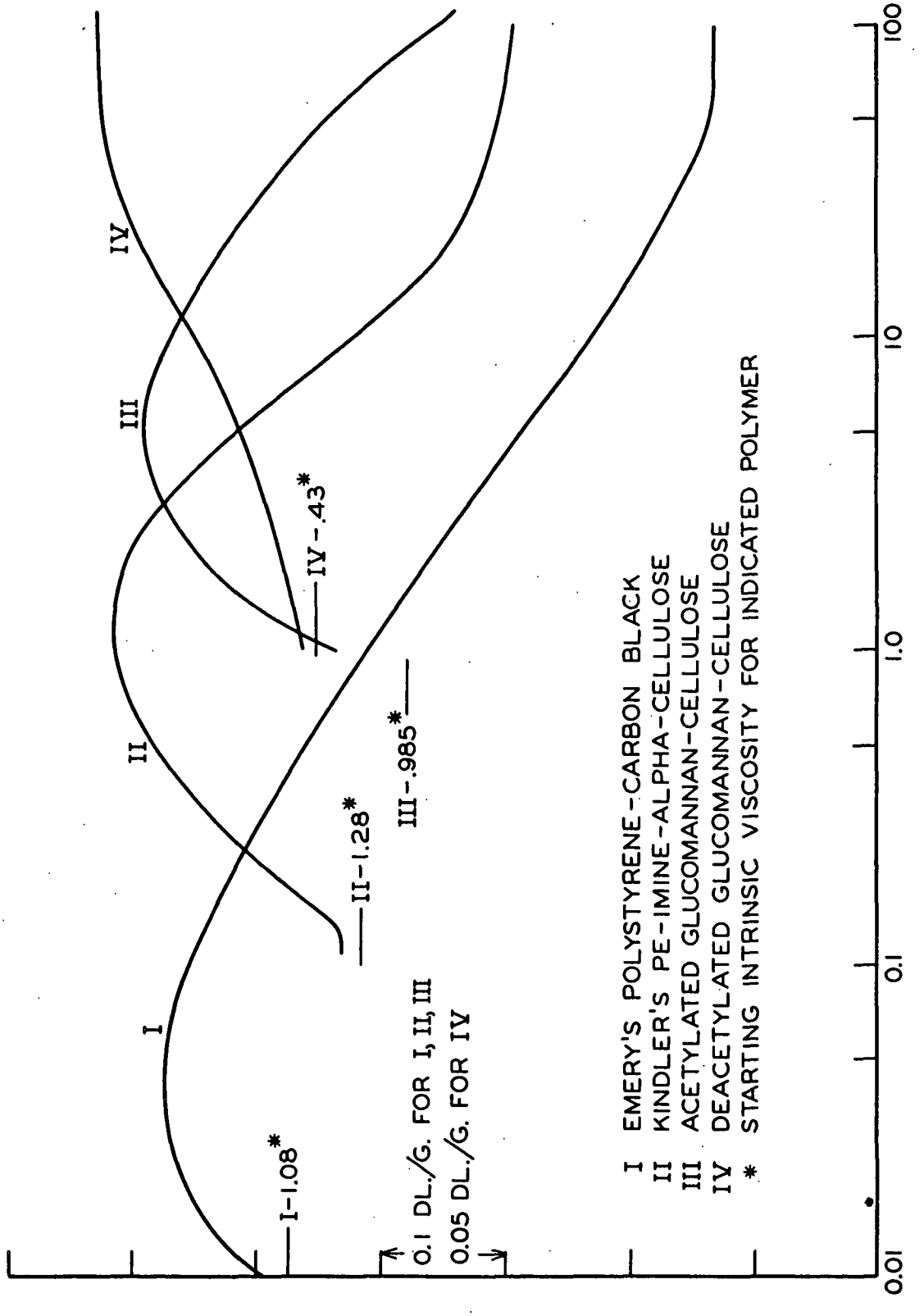

Figure 17. Intrinsic Viscosity Versus Time for the Bulk Phases of Four Different Systems

BEHAVIOR OF GLUCOMANNAN DURING PULPING

It has been substantiated that the removal of glucomannan acetyl leads to decreased solubility and increased sorption of the glucomannan onto a cellulose substrate. These results can be combined with results obtained by other workers to develop theories concerning the behavior of glucomannan during pulping.

Luce (41) has measured the distribution of glucomannan across the cell walls of both kraft and sulfite softwood fibers by a chemical method. He found that the kraft fibers have a high concentration of glucomannan on the surface while the sulfite fibers have uniform glucomannan through the cell wall. It should be mentioned that various investigators (42-44) have indicated that the distribution of mannose in the cell wall prior to cooking is quite uniform with, perhaps, a slight increase proceeding from the primary wall to the lumen.

These distributions can be explained with respect to glucomannan acetyl content. In the case of the kraft pulp, the glucomannan is deacetylated and dissolved by the high pH cooking liquor. Near the end of the cook, as the pH lowers, glucomannan remaining in the cooking liquor becomes less soluble and sorbs onto the cellulose. Unfortunately, a large amount of the glucomannan is degraded before cook pH conditions favor sorption. During sulfite pulping, the glucomannan is not deacetylated and a large portion then dissolves in the cooking liquor. Apparently, a portion of the glucomannan is of such a high molecular weight or so oriented that it is not dissolved during cooking. The high solubility of the glucomannan in the acid cooking liquor, combined with acid degradation, leads to no appreciable sorption of dissolved glucomannan onto the cellulose surface. Thus, the glucomannan remaining in sulfite pulp probably was not dissolved and resorbed during cooking.

The glucomannan content of sulfite pulp can be increased by a neutral or high pH precook. These experiments have been described earlier in this dissertation.

Several workers (21, 47) have investigated this procedure, and it is generally agreed that the glucomannan is stabilized by acetyl removal. The conditions of the precook are such (pH of 4 to 11) that solubility of the deacetylated glucomannan would not be expected during the precook. Annergren and Rydholm (20) carried out precooks in the presence of cotton linters and detected no pick-up of glucomannan during the precook. Croon, et al. (21) found that acetyl groups are removed during the precook over a pH range of 4 to 11 (lower pH precooks required higher temperature and longer times). No information is available concerning distribution of the hemicellulose in a two-stage sulfite fiber.

Croon, et al. (21) hypothesize that removal of bulky acetyl groups leads to closer packing and a higher degree of order which, in turn, decreases the susceptibility of the polymer to acid hydrolysis. Experimental results obtained by this writer indicate that a solubility effect may be involved. It is felt that the glucomannan is deacetylated in the first stage with no significant dissolution into the liquor. During the low pH stage the deacetylated glucomannan resists dissolving (quite like the undissolved material in a regular sulfite cook) and a significantly greater portion is retained than during acid sulfite cooking. The fact that these two-stage pulps beat like sulfite rather than kraft pulps indicates that the glucomannan is probably distributed through the fiber wall.

While glucomannan acetyl content can be used to explain pulping behavior in the above illustrations, there are examples in which the role of the acetyl group is not clear. Annergren and Rydholm (19) found that a slow (weekend), low-temperature (70 to 80°C.), sulfite cook (Mitscherlich) has a similar increase in glucomannan content. While these authors have not published results concerning acetyl removal, Thompson (45) found that acetyl groups are not removed by this cooking procedure. This glucomannan retention may possibly be explained by a rearrangement of the glucomannan to a more ordered association with the cellulose, making the glucomannan

more resistant to acid hydrolysis and dissolution. Thompson (45) suggests that a migration of acetyl groups to the primary hydroxyl position, a distinct possibility in the presence of acid, may bring about a configurational change in the glucomannan similar to deacetylation. Linnell (35) hypothesizes that lignin-carbohydrate bonds exist and that increased glucomannan retention in two-stage cooks may be due to the breaking of these bonds during the precook, which prevents the lignosulfonates from pulling the glucomannan into solution during the second stage.

EFFECT OF ACETYL CONTENT ON REFINING AND PAPERMAKING PROPERTIES OF COTTON-LINTER PULPS

Because it was anticipated that the presence of glucomannan, acetylated or deacetylated, would enhance the papermaking properties of the cotton linters and because this effect was so pronounced; discussion in this section will be limited to comparing the acetylated and deacetylated glucomannans, except for one point concerning refining. Whenever refining and hemicelluloses are discussed, it is usually stated that the hemicelluloses help to swell the fibers making them more plastic and amenable to the physical action of refining (46). This then leads to fibrillation rather than cutting. Within limits, the more hemicellulose, the faster the pulp beats. Consideration is also given the kind of hemicellulose, the number of available hydroxyl groups, presence of hydrophilic groups, and other similar properties. No mention is made of the location, or distribution, of the hemicellulose in the pulp. Luce (41) found that kraft pulp has most of the hemicellulose on the surface, while in sulfite it is uniformly distributed. While hemicellulose on the fiber surface may be more instrumental in increasing strength properties, a uniform distribution should enhance plasticization and flexibility of the pulp. In the refining study carried out in this thesis, glucomannan was sorbed onto the surface of the fibers. While there was a freeness decrease prior to refining (chemical beating), the rate of freeness decrease during refining was

not affected by the presence of the glucomannan. In a sense, the presence of the glucomannan merely gave the refining procedure a 15-minute headstart. Perhaps, part of the reason that a sulfite pulp beats faster than a kraft pulp is related to hemicellulose distribution.

In comparing the strength properties of pulps containing acetylated and deacetylated glucomannan, it should be pointed out that other factors beside acetyl content may be important. If the glucomannan-cellulose association is considered to be one of the direct consequences of acetyl content, the only difference except acetyl content would be quantity of glucomannan sorbed and its number average molecular weight. The pulp containing deacetylated glucomannan had polymer with a molecular weight approximately 10% higher than the acetylated glucomannan. It is not believed that this difference would measurably affect handsheet strength properties.

The handsheet strength properties evaluated were tear factor, breaking length, stretch, and tensile energy absorption. For all of these properties, the pulp containing deacetylated glucomannan had significantly higher strength values over the freeness range considered. This indicates that the presence of acetyl groups in the glucomannan tends to decrease its efficiency as a beater additive.

It may seem contradictory that the tear strength values are higher in the case of the deacetylated glucomannan. However, if the deacetylated glucomannan is a more efficient hydrophilic agent or a better plasticizing aid, less cutting or fiber deterioration would be expected at a given freeness level. Tear and stretch values, being related to individual fiber strength, might very well be lower in the case of the acetylated glucomannan due to more severe degradation of the fibers, while breaking length and tensile energy absorption would be lower because of less fiber bonding and poorer bond distribution.

CONCLUSIONS

The presence of acetyl groups on natively acetylated glucomannan greatly influences the behavior of this polymer. Removal of these groups leads to decreased solubility and higher rates of sorption onto a cotton-linter substrate. In the case of the acetylated glucomannan, the amount sorbed tends toward a maximum of approximately 7.5% of the cotton-linter weight over the range of addition investigated. It is believed that the sorption is restricted to monolayer coverage. The deacetylated glucomannan, however, has a higher specific sorption at a given addition than the acetylated glucomannan and is characterized by no sorption limit. In this case, it is felt that multilayer sorption occurs.

No fractionation with respect to acetyl content occurred during the sorption runs. Because a random acetyl distribution was present, no conclusions can be drawn concerning this point.

The sorption of both the acetylated and deacetylated glucomannan was characterized by the initial sorption of smaller molecules. This indicates that diffusion is prominent in the sorption mechanism. After mass equilibrium, larger acetylated molecules continued to replace smaller ones on the surface of the cellulose as the system tended toward thermodynamic equilibrium. This exchange was not apparent in the case of the deacetylated polymer.

It was also determined that for pulps containing equal amounts of sorbed glucomannan, the one with the deacetylated glucomannan exhibited higher tearing strength, breaking length, and tensile energy absorption as well as greater stretch at given freeness levels. This indicates that the presence of acetyl groups has a deleterious effect on the polymer's efficiency as a beater additive.

ACKNOWLEDGMENTS

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APPENDIX I

DEGRADATION OF THE GLUCOMANNAN TO THE DESIRED MOLECULAR WEIGHT

Preliminary experiments concerning the glucomannan degradation indicated that agitation, increase in temperature, and increase in initial salep concentration increase the rate of enzyme action.

The first approach to producing glucomannan with the desired molecular weight was concerned with relating time of enzyme action to cuene intrinsic viscosity of the product. The trial was carried out by dispersing 60 grams of Tubera salep in 2500 ml. of distilled water at 70°F. After various time intervals samples were taken, the insoluble material removed by centrifugation, and the glucomannan isolated by solvent exchange from water to acetone to petroleum ether. The intrinsic viscosities were then determined in cuene at 30°C. using Cannon-Ubbelohde semimicro dilution viscometers (either no. 50, 75, or 100).

Results of this enzyme degradation are listed in Table IX. Figure 18 illustrates the intrinsic viscosity as a function of time. The zero time sample was obtained by first deactivating the enzyme by refluxing Tubera salep in methyl alcohol for five hours and then extracting the glucomannan. From Fig. 18, it was determined that a hydrolysis time of from 40 to 44 hours would give a product with the desired intrinsic viscosity (0.35 to 0.45).

TABLE IX

CUENE INTRINSIC VISCOSITIES FOR VARIOUS TIMES OF ENZYME ACTION

Sample	Time, hr.	Intrinsic Viscosity, dl./g.
1	27	0.94
2	52	0.25
3	73	0.15
4	100	0.12
5	143	0.09
6	0	3.30

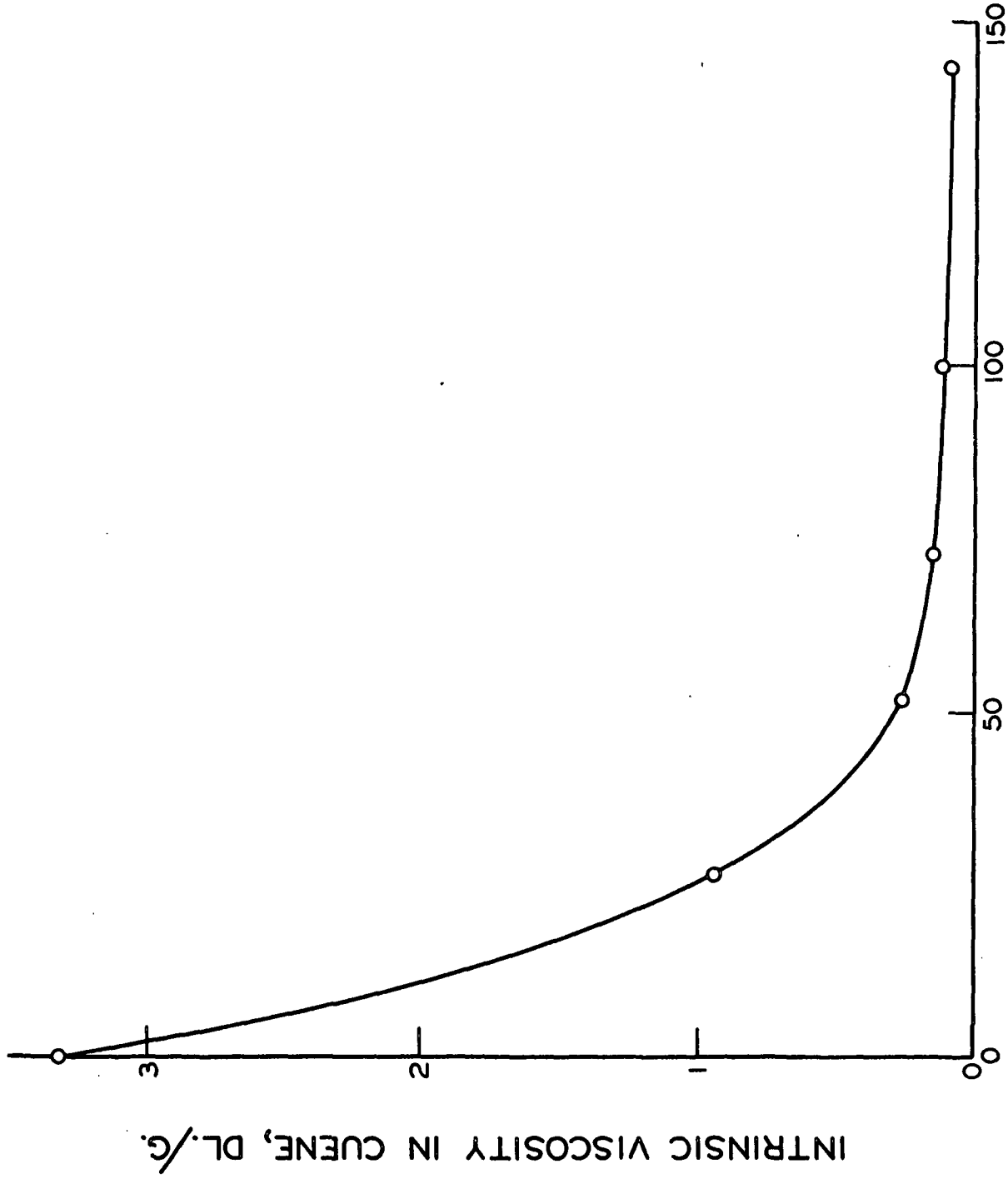

Figure 18. Intrinsic Viscosity Versus Time for Trial Degradation

The first attempt to produce a large batch of glucomannan was carried out by dissolving 750 grams of powdered Tubera salep in 30 liters of distilled water at 70°F. Prior to salep addition an undetermined amount of ptyalin was added to the water in order to degrade any starch which may be present in the glucomannan. A Lightnin' mixer was used to agitate the solution during, and for 15 minutes after, the addition of the salep. Finally, a few drops of water saturated with xylene were added to the surface to retard microorganism growth. Extraction of the glucomannan and enzyme action were carried out in the dark.

After 35 hours, centrifugation of the solution was begun. This was carried out in the Beta-fuge at 25°C. A batch procedure was used which allowed centrifugation of no more than 1.5 liters. Each batch was centrifuged for ten minutes at 11,000 r.p.m. The glucomannan solution was then poured with mixing into 90 liters of acetone. The mixer was allowed to run for two hours with occasional stirring. The precipitated glucomannan was then isolated by siphoning off most of the acetone-water mixture and filtering off what remained. The glucomannan was then redispersed in 20 liters of acetone for 24 hours. This was then replaced with petroleum ether and allowed to sit for 48 hours. Finally, the glucomannan was isolated by filtering off as much of the ether as possible and then drying under vacuum for five days.

The glucomannan had an intrinsic viscosity of 1.4 which is much higher than that desired. Possible explanations for this high intrinsic viscosity could be the ten hours necessary for centrifugation, the use of xylene, or the size of the batch.

As time of enzyme action proved unsatisfactory for isolating a product of the desired cuene intrinsic viscosity, it was decided to relate solution absolute viscosity to intrinsic viscosity of the polymer. Such techniques as measuring

the solution efflux time with various viscometers proved unsuccessful due to the long time periods involved initially and the difficulty in handling highly viscous solutions. A tube and metal shots, on the other hand, as used for determining viscose viscosities, proved unsatisfactory because of the rapid rate of shot travel. It was finally found that a Hoeppler viscometer could provide a measure of the absolute viscosity of the solutions. Absolute viscosities are determined by timing the period of fall for various steel and glass balls through the solution and calculating the absolute viscosity according to the equation:

$$U = F\ (S_k - S_f)\ K \qquad (11),$$

with U being absolute viscosity in centipoises, F the period of fall in seconds, S_k and S_f the specific gravities of the ball and solution, respectively, and K a ball constant. For a specific ball, the period of fall would be a direct measure of absolute viscosity.

Pilot size batches of the Tubera salep were degraded in order to relate absolute viscosity to cuene intrinsic viscosity. The procedure consisted of dispersing 20 grams of the salep per liter of distilled water, allowing the water-soluble glucomannan to be extracted overnight, removing the insoluble residue by centrifugation, and sampling at various intervals. Simultaneously, the absolute viscosity of a sample was determined and a portion precipitated for cuene intrinsic viscosity determinations.

These results are summarized in Table X. Figures 19 and 20 are constructed from these data. Figure 19 indicates that there is a poor relationship between cuene intrinsic viscosity and absolute viscosity. Possible causes for this great scatter may be differences in ball properties and specific gravity when substituted into Equation (11). Cuene intrinsic viscosity also seems to fluctuate somewhat, compounding any difficulty. At lower levels of absolute viscosity (below 70) the

scatter is less and perhaps rheological properties of the solution are affected by viscosity level. If the actual period of fall for all samples measured with Ball "B" is plotted against cuene intrinsic viscosity, a better relationship is seen. Periods of fall with Ball "B" of from 10 to 30 seconds should correspond to intrinsic viscosities of from 0.4 to 0.6, respectively, for a 2% solution. As described in the experimental section of the thesis, this method was successful.

TABLE X

HOEPPLER VISCOMETER AND CUENE INTRINSIC VISCOSITY DATA

Sample	Time of Enzyme Action, hr.	Ball	Period of Fall, sec.	Absolute Viscosity, c.p.	Intrinsic Viscosity in Cuene, dl./g.
V-1	44.5	C	122.60	218.0	1.12
V-2	49.5	C	60.10	107.0	0.84
V-3	68.5	C	14.60	26.0	0.66
V-4	73.5	B	65.00	19.4	0.96
V-5	99.0	B	30.40	9.1	0.63
V-6	171.0	B	9.85	2.9	0.43
W-1	38.0	C	118.80	211.0	0.66
W-2	42.0	C	37.50	67.0	0.56
W-3	60.0	B	40.50	12.1	0.58
W-4	85.5	B	15.10	3.9	0.44
W-5	109.5	A	118.30	2.9	--
W-6	180.5	A	68.40	1.7	0.36

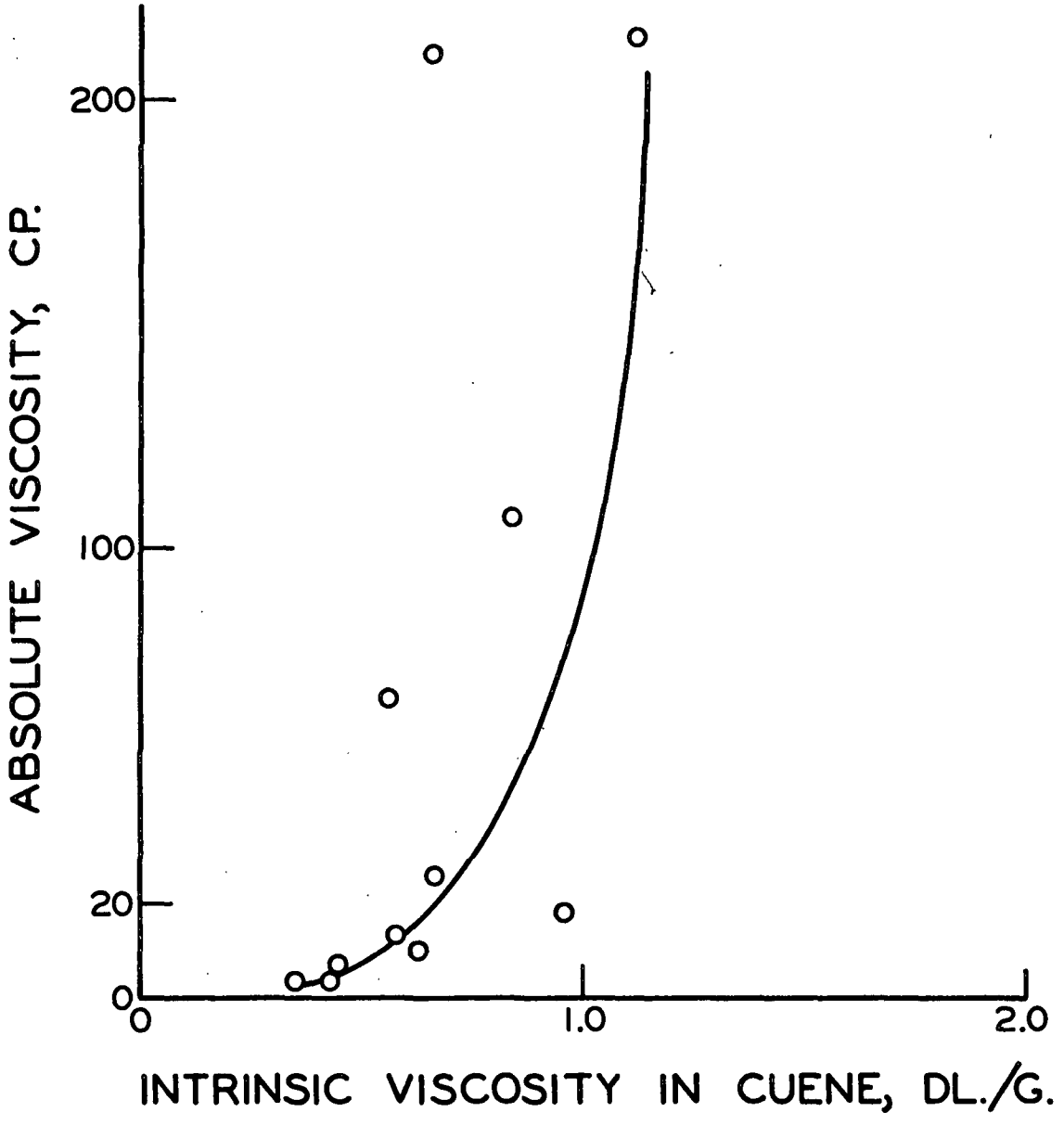

Figure 19. Absolute Versus Intrinsic Viscosity

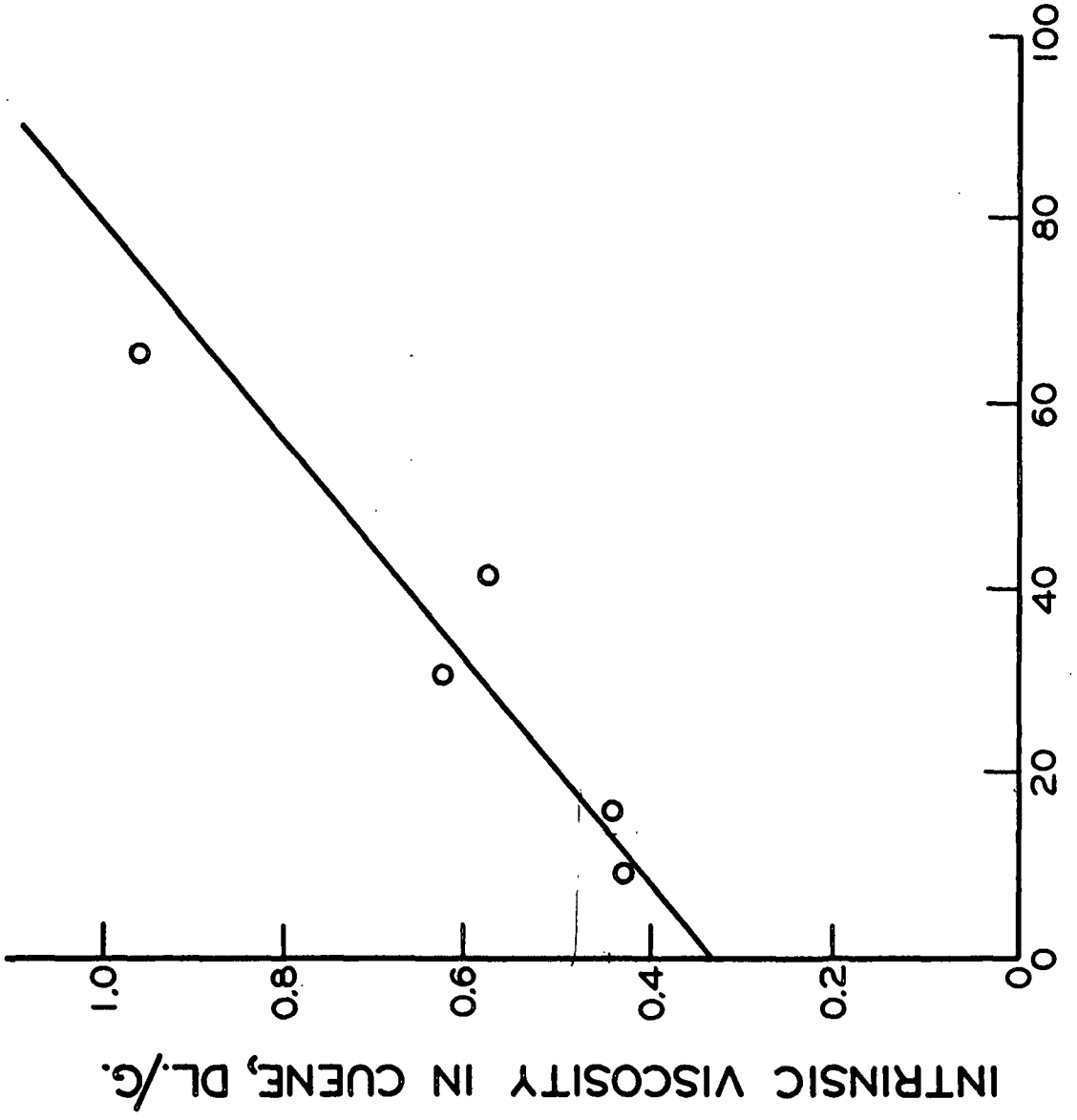

Figure 20. Cuene Intrinsic Viscosity as a Function of Period of Fall for Ball "B"

APPENDIX II

EXPERIMENTAL PROCEDURES

ACETYL DETERMINATIONS

Acetyl contents were determined by the transesterification method of Whistler and Jeanes (37) as described by Katz (1). The procedure was modified because of the high bulk of some samples and the small amounts of others available for analysis. Because of the high bulk of the glucomannan starting material, excess methanol was used to insure proper wetting. In other cases, when only small amounts of sample were available, more dilute acid and base were utilized in the procedure.

QUANTITATIVE SUGAR ANALYSIS

All quantitative sugar analyses reported in this thesis were carried out by the Analytical Department at The Institute of Paper Chemistry. The Saeman (38) paper chromatography technique was used to determine neutral sugars and Institute Method 25 was used to determine uronic acid content.

INTRINSIC VISCOSITY MEASUREMENTS

Intrinsic viscosity measurements were carried out in both 1.0% aqueous sodium chloride and 0.5M cuene.

1.0% SODIUM CHLORIDE AS A SOLVENT

Samples to be analyzed were weighed into volumetric flasks (2-10 ml., depending on the quantity available), the solvent was added, and the volumetric flasks were placed on a rotator overnight. Prior to the analyses, the solutions were adjusted to the proper volume and blown through coarse glass filter funnels.

Occasionally, the concentration of the solution was substantiated by the phenol-sulfuric acid colorimetric procedure. Close agreement was generally observed between the concentration determined by this method and that obtained by correcting the amount weighed out for moisture content. The samples dissolved quite readily and no residue was observed in the filter funnels.

Viscosity measurements were made with Cannon-Ubbelohde number 50 semimicro dilution viscometers at 30 ± 0.005°C. All dilutions were carried out with microsyringes fitted with Chaney adaptors. Examples of the extrapolations to give the intrinsic viscosities are shown in Fig. 21.

0.5M CUENE AS A SOLVENT

The procedure was modified somewhat in order to measure intrinsic viscosities in cuene. The samples were dispersed in water, allowed to rotate overnight, adjusted to the desired concentration with 1.0M cuene, and rotated an additional hour. Prior to viscosity measurements, the solutions and solvents were blown (with nitrogen) through coarse glass filter funnels. All vessels were flushed with nitrogen and great care was taken to minimize oxidative degradation. Examples of these extrapolations are shown in Fig. 22.

OSMOMETRY

The Mechrolab, Model 501, High Speed Osmometer provides a rapid, accurate technique for determining number average molecular weights of polymers in solution. Linnell (35) presents an excellent description of the mechanics and theory of this instrument.

It was the original intent to determine number average molecular weights on the glucomannan samples with distilled water as the solvent. After several unsuccessful attempts, however, it was established that reasonably good measurements

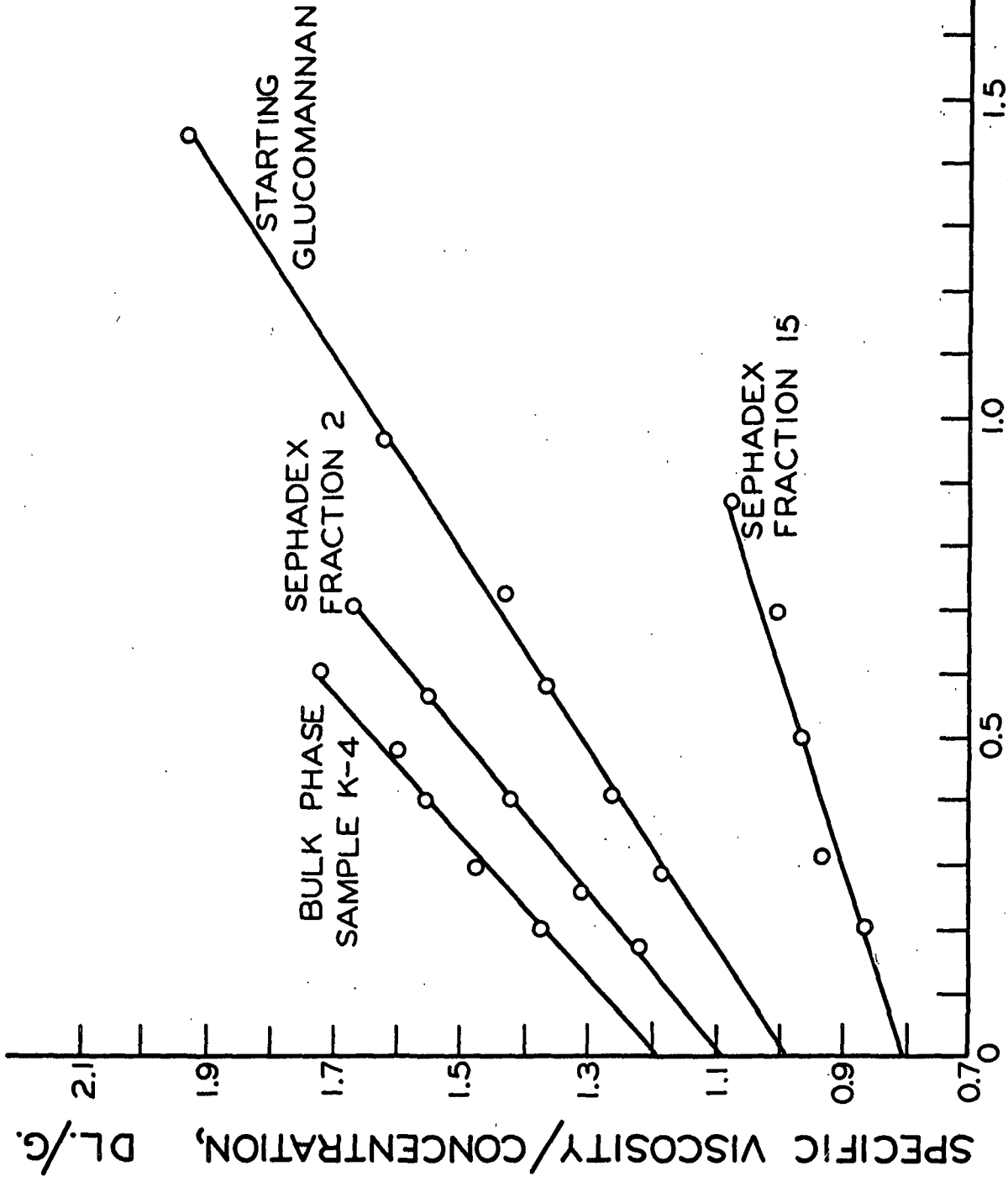

Figure 21. Examples of Extrapolations for Intrinsic Viscosity Determinations in 1% NaCl

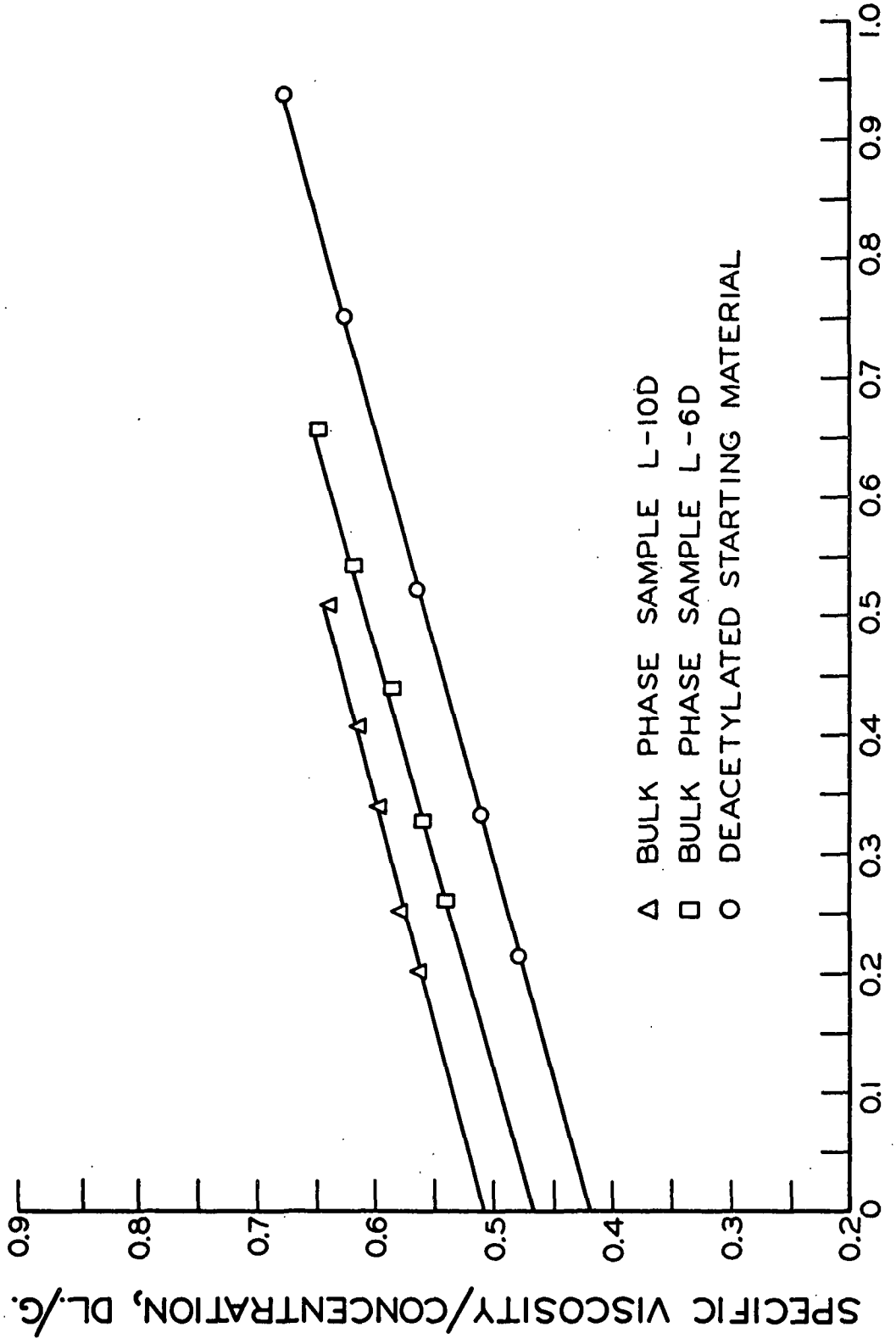

Figure 22. Examples of Extrapolations for Intrinsic Viscosity Determinations in Cuene

could be obtained by using 1.0% sodium chloride solvent with a few drops of Pluronic-L62 (Wyandotte Chemical Company) added per liter. It was important to coat the working parts of the osmometer with a more concentrated solution of this detergent. It was also found that it was necessary to use -07 membranes (normally recommended for organic solvents) and extremely dilute solutions. Even with these modifications, diffusion of the polymer through the membrane created problems with the lower weight fractions. The extrapolations used to determine molecular weight are shown in Fig. 23.

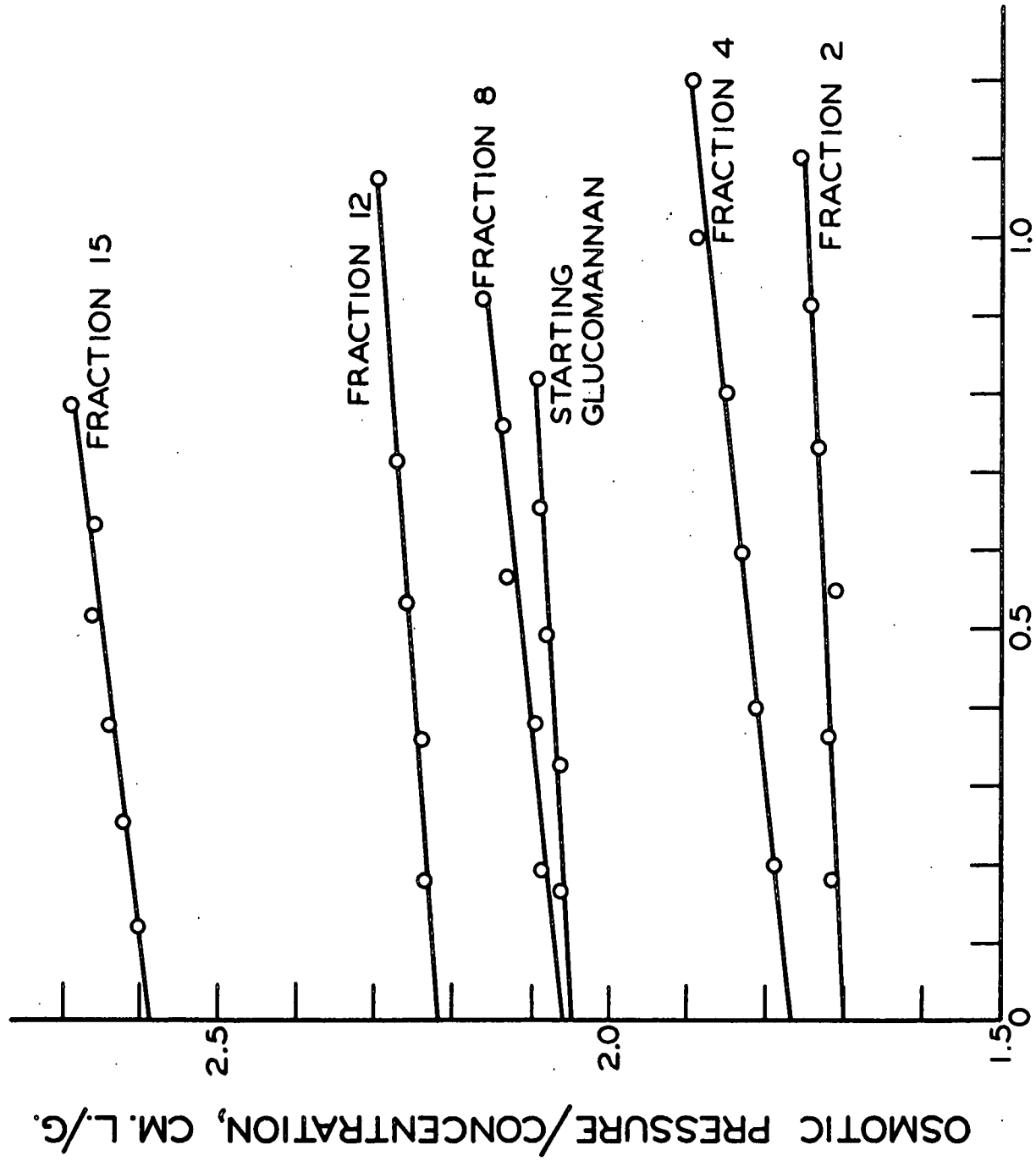

Figure 23. Osmotic Pressure Extrapolations

APPENDIX III

PHENOL-SULFURIC ACID COLOR REACTION

A standard curve for calculating the concentration of glucomannan in solution by the phenol-sulfuric acid color reaction has been constructed. A standard solution was prepared by making up a 1% solution of glucomannan in distilled water. A moisture correction indicated an actual concentration of 0.88%. The concentration of the standard solution was verified further by pipetting 10-ml. samples of the solution into tared weighing bottles, freezing, freeze-drying, oven drying (60°C.) under vacuum, and reweighing. This method indicated a glucomannan concentration of 0.8415 $\pm$ 0.0005%.

In order to form a standard curve of absorbance versus concentration, a technique modified after Dubois, et al. (34) was utilized. The standard solution was diluted over a range of from 20 to 100 micrograms per ml. Duplicate absorbance measurements were then made at each dilution. According to the procedure used, 2 ml. of a sample are placed in a small beaker to which 1 ml. of 5% phenol is added. Then 5 ml. of concentrated sulfuric acid are rapidly added. The latter step hydrolyzes the polymer which then reacts with the phenol to produce a yellow color. Absorbance measurements are made on a DU Beckman spectrophotometer at a wavelength of 490 nm. Each sample is run in duplicate.

Figure 24 illustrates the relationship of concentration to absorption. During the sorption measurements, frequent checks were made with known solutions to substantiate the curve. Removal of acetyl groups did not affect the relationship. Sorption measurements on duplicate samples usually varied by no more than 1%.

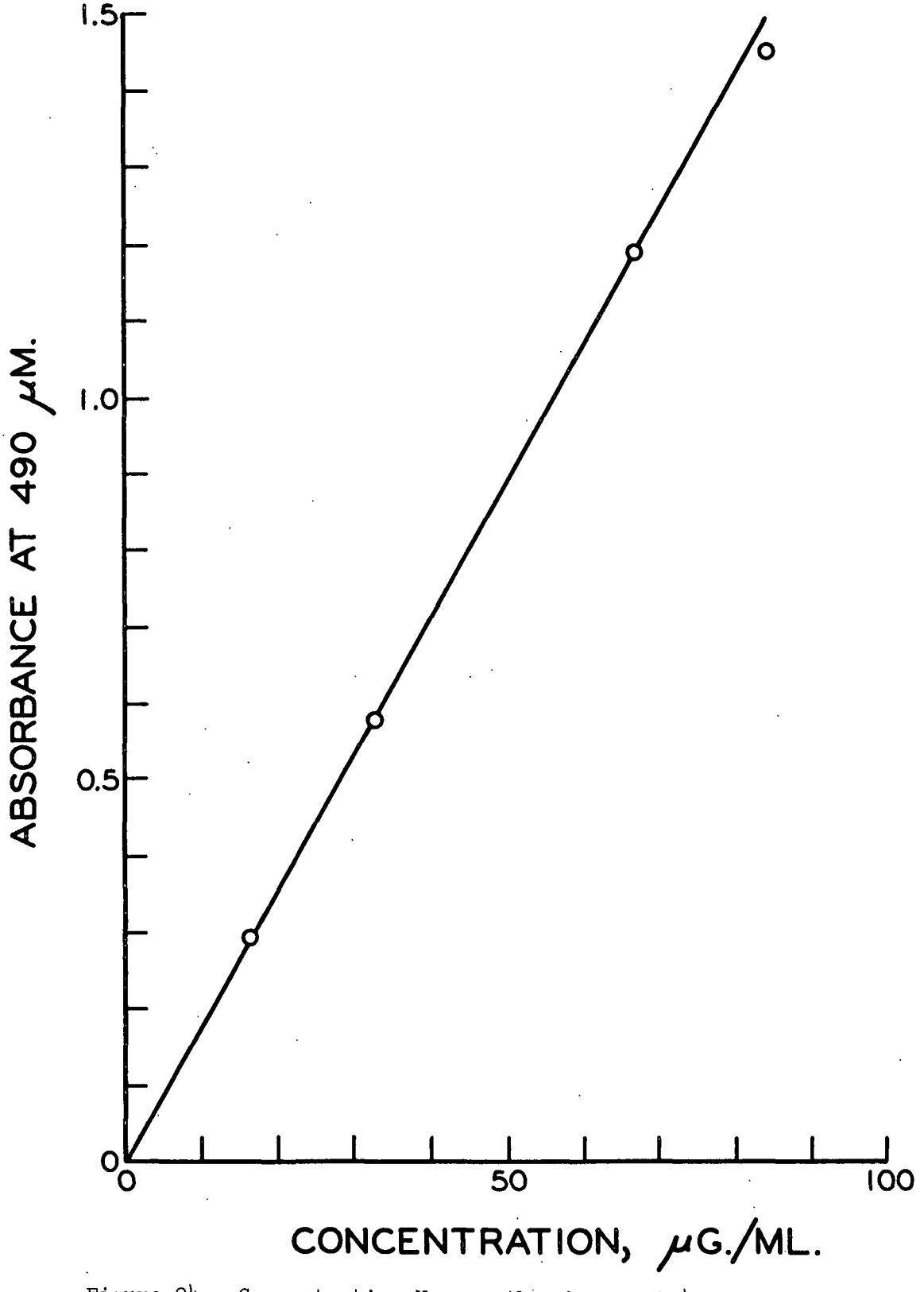

Figure 24. Concentration Versus Absorbance at 490 nm. for Glucomannan by the Phenol-Sulfuric Acid Colorimetric Method

APPENDIX IV

SOME EXPERIMENTAL RESULTS

This appendix contains experimental results not placed in the body of the thesis because the data are given graphically when discussed.

TABLE XI

RATE DATA FOR ACETYLATED, DEACETYLATED, AND PARTIALLY DEACETYLATED GLUCOMANNANS

Sorption Run F
Pulp Consistency = 0.68%

	Acetylated (2.75%)	Deacetylated	1.15% Acetyl	1.77% Acetyl
Glucomannan added, % of cotton linter weight	10.4	9.7	10.3	9.9
Time, hr.	Specific Sorption, % of cotton linter wt.	Specific Sorption, % of cotton linter wt.	Specific Sorption, % of cotton linter wt.	Specific Sorption, % of cotton linter wt.
1	4.09	6.20	4.70	4.52
6	5.48	7.68	5.99	6.09
11	5.58	8.12	6.18	6.08
18	5.97	8.15	6.49	6.39
24	6.29	8.51	6.61	6.51
41	6.98	8.32	7.47	7.12
49	7.18	8.57	7.35	7.39
94	7.02	8.69	--	--

TABLE XII

RATE DATA FOR ACETYLATED AND DEACETYLATED GLUCOMANNAN

Sorption Run E

Acetylated (10.2% addition)			Deacetylated (9.4% addition)	
Sample	Specific Sorption, % of cotton linter weight	Time, hr.	Sample	Specific Sorption, % of cotton linter weight
E-1	3.67	1.08	E-1D	5.46
E-2	5.46	4.00	E-2D	6.53
E-3	5.54	8.38	E-3D	7.95
E-4	5.98	20.00	E-4D	8.47
E-5	6.27	25.50	E-5D	8.15
E-6	6.85	43.70	E-6D	8.12
E-7	7.12	56.25	E-7D	8.11
E-8	6.65	95.50	E-8D	7.68

Sorption Runs K and L

Acetylated (14.85% addition)			Deacetylated (14.30% addition)		
Sample	Specific Sorption, % of cotton linter weight	Time, hr.	Sample	Specific Sorption, % of cotton linter weight	Time, hr.
K-2	4.02	1.0	L-1D	3.55	1.0
K-3	5.51	3.0	L-2D	6.91	2.0
K-4	5.85	5.0	L-3D	8.03	3.0
K-5	6.20	8.0	L-4D	8.40	5.0
K-6	6.51	12.0	L-5D	9.50	8.0
K-7	6.79	18.0	L-6D	10.58	12.0
K-8	7.12	24.0	L-7D	11.33	18.0
K-9	7.31	30.0	L-8D	11.38	24.0
K-11	7.41	40.0	L-9D	11.45	36.0
K-12	7.43	48.0	L-10D	11.47	48.0
K-13	7.44	60.0	L-11D	11.42	70.0
K-14	7.41	79.0	L-12D	11.55	84.0
K-15	7.39	93.0	L-13D	11.50	96.0
K-16	7.43	109.0			

TABLE XIII

EFFECT OF INITIAL DEACETYLATED GLUCOMANNAN CONCENTRATION ON AMOUNT SORBED AT EQUILIBRIUM

Sample	Glucomannan Added, % of cotton linter weight	Specific Sorption, % of cotton linter weight
M-1	2.856	2.59
M-2	5.712	5.15
M-3	8.568	7.713
M-4	14.280	11.89
M-5	21.420	17.38
M-6	28.560	21.61
L-11D	14.3	11.42
E-D	9.4	8.14
F-D	9.8	8.5

TABLE XIV

INTRINSIC VISCOSITIES AND MOLECULAR WEIGHTS OF BOTH SUPERNATANT AND SORBED POLYMER AT TIMES DURING SORPTION RUNS[a]

Sample[b]	Time of Sorption, hr.	Specific Sorption, % cotton linter wt.	Intrinsic Viscosity[c] Bulk	Intrinsic Viscosity[c] Surface	Number Average Molecular Weight Bulk	Number Average Molecular Weight Surface
K- starting material	--[d]	--	0.985		15,790	
K-1		2.05	1.01	0.758	16,376	10,678
K-2	1	4.02	1.08	0.763	18,120	10,785
K-3	3	5.51	1.09	0.833	18,371	12,294
K-4	5	5.85	1.19	0.722	20,930	9,931
K-5	8	6.20	1.18	0.754	20,672	10,594
K-6	12	6.51	1.18	0.774	20,672	11,018
K-7	18	6.79	1.14	0.833	19,638	12,294
K-8	24	7.12	1.13	0.855	19,081	12,789
K-9	30	7.31	1.11	0.881	18,871	13,367
K-11	40	7.41	1.08	0.897	18,120	13,731
K-12	48	7.43	1.06	0.923	17,620	14,330
K-13	60	7.44	1.04	0.940	17,119	14,725
K-14	79	7.41	0.99	0.982	15,909	15,718
K-15	93	7.39	0.92	1.036	14,260	17,022
K-16	109	7.43	0.91	1.031	14,029	16,909
L-starting material	--	--	0.430		16,502	
L-1D	1	3.55	0.435	0.4135	16,790	15,932
L-2D	2	6.91	0.441	0.4180	17,139	15,821
L-3D	3	8.03	0.445	0.4175	17,327	15,792
L-4D	5	8.40	0.444	0.4200	17,311	15,935
L-5D	8	9.50	0.457	0.4170	18,076	15,763
L-6D	12	10.58	0.469	0.4170	18,789	15,763
L-7D	18	11.33	0.477	0.4180	19,269	15,821
L-8D	24	11.38	0.493	0.4130	20,244	15,543
L-10D	48	11.47	0.510	0.4110	21,294	15,429
L-12D	84	11.55	0.503	0.4130	20,857	15,542
L-13D	96	11.50	0.505	0.4120	20,983	15,484

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a See Fig. 5 for the rate curve.

b Samples K-1 to K-16 are acetylated, while L-1D to L-13D are deacetylated.

c dl./g.; K samples in 1% sodium chloride, L samples in cuene.

d Shaken and isolated.

TABLE XV

HANDSHEET STRENGTH PROPERTIES

Sample	Refining Time, min.	Freeness S.-R., ml.	Basis Weight, g./m.^{2}	Density, g./ml.	Tear Factor, g./100 g.	Breaking Length, m.	Stretch[a]	T.E.A.[b]	E.M.C.[c]
Cotton linters	0	880	64.10	0.473	96.7	1939.6	2.29	0.0242	6.94
	15	685	63.50	0.575	79.5	2896.9	1.97	0.0286	7.30
	30	465	57.90	0.645	38.9	3202.3	1.38	0.0188	7.37
Cotton linters plus acetylated glucomannan	0	720	64.55	0.490	99.1	2746.9	4.42	0.0638	6.78
	15	510	67.10	0.624	80.5	4386.4	3.20	0.0765	7.02
	30	275	61.75	0.715	61.5	5047.2	2.43	0.0606	7.20
Cotton linters plus deacetylated glucomannan	0	740	65.3	0.490	104.1	3061.2	4.72	0.0760	7.20
	15	450	62.45	0.624	78.5	4818.7	3.33	0.0812	7.15
	30	240	56.75	0.707	59.9	5224.1	2.45	0.0588	7.28

[a] Percent elongation.

[b] Tensile energy absorption, kg. cm./cm.^{2}.

[c] Equilibrium moisture content, % (73°F., 50% R.H.).

APPENDIX V

THE EFFECT OF PHENYLMERCURIC ACETATE ADDITION ON SORPTION

The effect of phenylmercuric acetate on sorption was evaluated so that its use as a bacteria-retarding agent could be considered. A long-term sorption run was carried out using samples containing 1, 5, and 10 p.p.m. of this chemical. Rate curves are illustrated in Fig. 25.

These results indicate that the presence of phenylmercuric acetate influences the sorption behavior of the glucomannan and, therefore, its use was not considered further.

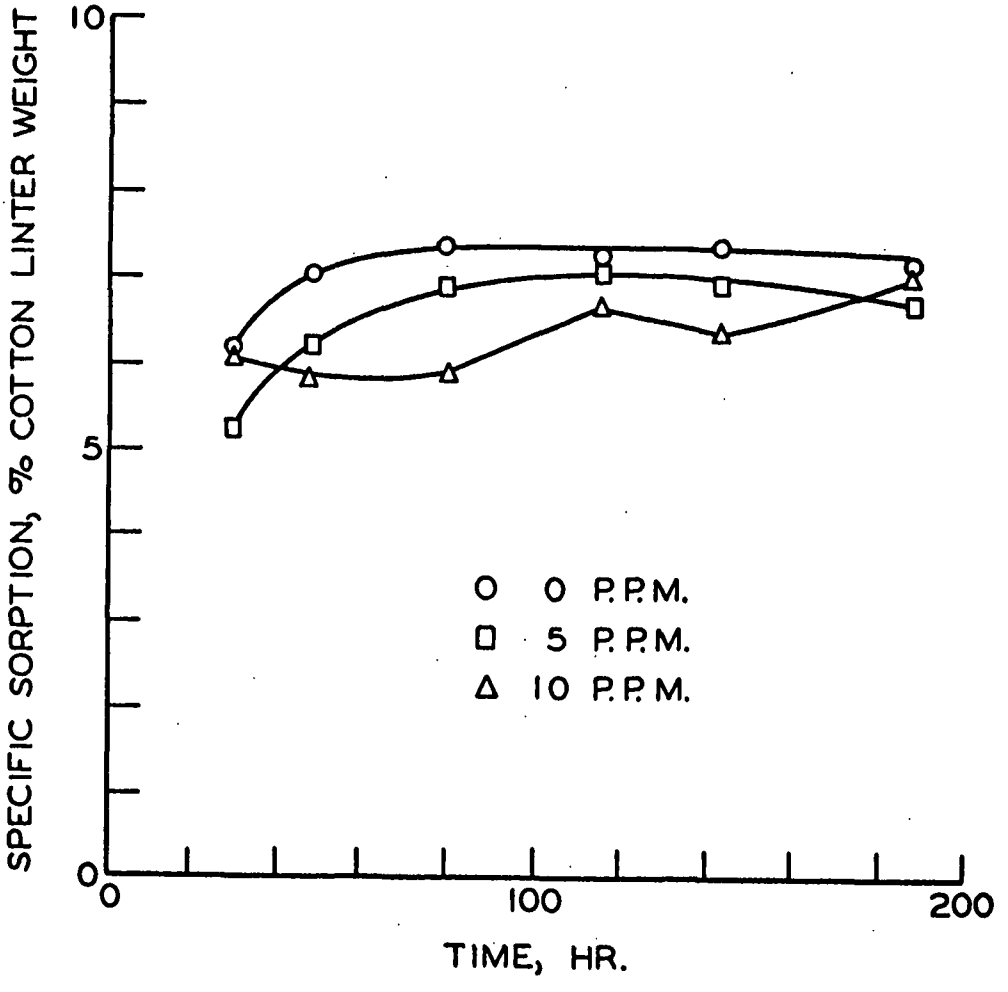

Figure 25. Effect of Phenylmercuric Acetate on Glucomannan Sorption

APPENDIX VI

BEATING PROCEDURE USED WITH SMALL PULP SAMPLES

1. The pulp sample was dispersed for 300 counts in a British disintegrator.

2. It was then dewatered to 6% consistency.

3. Samples of the proper size for Schopper-Riegler freeness were then weighed out, the freeness measured, the pulp reclaimed, dewatered to the original weight, and mixed thoroughly back into the pulp sample.

4. A sample of the proper size for four standard handsheets was then withdrawn.

5. The remaining pulp was beaten in a Jokro mill for 15 minutes.

6. Steps one to five were repeated to obtain a 15-minute sample.

7. Steps one to four were repeated to obtain a 30-minute sample.